NASA-CR-198567

Japanese Technology Evaluation Center

JTEC

JTEC Panel Report on

Separation Technology In Japan

C. Judson King, Chair
Edward L. Cussler
William Eykamp
George E. Keller II
H.S. Muralidhara
Milton E. Wadsworth

March 1993

(NASA-CR-198567) JTEC PANEL REPORT ON SEPARATION TECHNOLOGY IN JAPAN Final Report (Loyola Coll.) 163 p

N95-71515

Unclas

Z9/25 0049779

International Technology Research Institute
Michael J. DeHaemer JTEC/WTEC Director
Geoffrey M. Holdridge JTEC/WTEC Series Editor

Loyola College in Maryland
4501 North Charles Street
Baltimore, Maryland 21210-2699

JAPANESE TECHNOLOGY EVALUATION CENTER

SPONSOR The Japanese Technology Evaluation Center (JTEC) is operated for the Federal Government to provide assessments of Japanese research and development (R&D) in selected technologies. The National Science Foundation (NSF) is the lead support agency. Paul Herer, Senior Advisor for Planning and Technology Evaluation, is NSF Program Director for the project. Other sponsors of JTEC include the National Aeronautics and Space Administration (NASA), the Department of Commerce (DOC), the Department of Energy (DOE), the Office of Naval Research (ONR), the Defense Advanced Research Projects Agency (DARPA), the U.S. Air Force, and the U.S. Army.

PURPOSE JTEC assessments contribute to more balanced technology transfer between Japan and the United States. The Japanese excel at acquisition and perfection of foreign technologies, whereas the U.S. has relatively little experience with this process. As the Japanese become leaders in research in targeted technologies, it is essential that the United States have access to the results. JTEC provides the important first step in this process by alerting U.S. researchers to Japanese accomplishments. JTEC findings can also be helpful in formulating governmental research and trade policies.

APPROACH The assessments are performed by panels of about six U.S. technical experts. Panel members are leading authorities in the field, technically active, and knowledgeable about both Japanese and U.S. research programs. Each panelist spends about one month of effort reviewing literature and writing his/her chapter of the report on a part-time basis over a twelve-month period. All recent panels have conducted extensive tours of Japanese laboratories. To provide a balanced perspective, panelists are selected from industry, academia, and government.

ASSESSMENTS The focus of the assessments is on the status and long-term direction of Japanese R&D efforts relative to those of the United States. Other important aspects include the evolution of the technology and the identification of key researchers, R&D organizations, and funding sources.

REPORTS The panel findings are presented to workshops where invited participants critique the preliminary results. Final reports are distributed by the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, Virginia 22161 (703-487-4650). Panelists also present their findings in conference papers, journals, and books. All results are unclassified and public.

STAFF The Loyola College JTEC staff helps select topics to be assessed, recruits experts as panelists, organizes and coordinates panel activities, provides literature support, organizes tours of Japanese labs, assists in the preparation of workshop presentations and in the preparation of reports, and provides general administrative support. Mr. M. Gene Lim of SEAM International provided literature support and advance work for this panel.

Dr. Michael J. DeHaemer
Principal Investigator
Loyola College
Baltimore, MD 21210

Mr. Geoff Holdridge
JTEC/WTEC Staff Director
Loyola College
Baltimore, MD 21210

Dr. George Gamota
Senior Advisor to JTEC
Mitre Corporation
Bedford, MA 01730

JTEC Panel on

SEPARATION TECHNOLOGY IN JAPAN

FINAL REPORT

March 1993

C. Judson King, Chair
Edward L. Cussler
William Eykamp
George E. Keller II
H.S. Muralidhara
Milton E. Wadsworth

This material is based upon work supported by the National Science Foundation (NSF) and the Department of Energy under NSF Grant ENG-9111333, awarded to the Japanese Technology Evaluation Center at Loyola College in Maryland. The Government has certain rights in this material. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation, the United States Government, the authors' parent institutions, or Loyola College.

Abstract

This is the final report of the JTEC Panel on Separation Technology in Japan. The study was sponsored by the National Science Foundation with additional support from the Department of Energy. It examines the state of the art of research and development in separation technology in Japan in comparison to that in the United States. The report includes an executive summary, introduction and analysis of major issues, and detailed chapters on separation and purification of gases, water purification, separations involving liquids, hydrometallurgical separations, ion-exchange membrane technology, dewatering and crystallization. Site reports on the visits that the panel made to Japanese corporate, government, and university laboratories are included as appendices. The report is based on these site visits and a literature review. The panel found that Japan is strong and highly competitive in several areas of separations. This position has been achieved for the most part, not by invention or creative new departures, but by careful selection of the most effective technology available on the world market, followed by diligent implementation, evolutionary advances, strong emphasis on management and control of quality, and effective use of corporate experience.

International Technology Research Institute at Loyola College

R. D. Shelton, Director

JTEC/WTEC STAFF

Michael J. DeHaemer, Principal Investigator, Director
Geoffrey M. Holdridge, Staff Director and JTEC/WTEC Series Editor
Bobby A. Williams, Assistant Director
Yvonne A. Lilley, Senior Secretary
Catrina M. Foley, Secretary
Aminah Batta, Editorial Assistant
Arnett J. Holloway, Editor

Advance Work in Japan Performed by M. Gene Lim of SEAM International

Copyright 1993 by Loyola College in Maryland. The U.S. Government retains a nonexclusive and nontransferable license to exercise all exclusive rights provided by copyright. This report is distributed by the National Technical Information Service (NTIS) of the U.S. Department of Commerce as NTIS Report # PB93-159564. Information on ordering from NTIS is available by calling (703) 487-4650.

FOREWORD

This report is one in a series of reports prepared through the Japanese Technology Evaluation Center (JTEC), sponsored by the National Science Foundation (NSF) and administered by Loyola College in Maryland. The report describes research and development efforts in Japan in the area of separation technologies.

Over the past decade, the United States' competitive position in world markets for high-technology products appears to have eroded substantially. As U.S. technological leadership is challenged, many government and private organizations seek to set policies that will help maintain U.S. competitive strengths. To do this effectively requires an understanding of the relative position of the United States and its competitors. Indeed, whether our goal is competition or cooperation, we must improve our access to the scientific and technical information in other countries.

Although many U.S. organizations support substantial data gathering and analysis directed at other nations, the government and privately sponsored studies that are in the public domain tend to be "input" studies. That is, they measure expenditures, personnel data, and facilities, but do not assess the quality or quantity of the outputs obtained. Studies of the outputs of the research and development process are more difficult to perform since they require a subjective analysis by individuals who are experts in the relevant technical fields.

The National Science Foundation staff includes professionals with expertise in a wide range of technologies. These individuals have the technical expertise to assemble panels of experts who can perform competent, unbiased, scientific and technical reviews of research and development activities. Further, a principal activity of the Foundation is the review and selection for funding of research proposals. Thus the Foundation has both experience and credibility in this process. The JTEC activity builds on this capability.

Specific technologies, such as displays, telecommunications, or biotechnology, are selected for study by individuals in government agencies that are able to contribute to the funding of the study. A typical assessment is sponsored by two or more agencies. In cooperation with the sponsoring agencies, NSF selects a panel of experts who will conduct the study. Administrative oversight of the panel is provided by Loyola College in Maryland, which operates JTEC under an NSF grant.

Panelists are selected for their expertise in specific areas of technology and their broad knowledge of research and development in both the United States and in Japan. Of great importance is the panelists' ability to produce a comprehensive, informed and unbiased report. Most panelists have travelled previously to Japan or have professional associations with their expert counterparts in Japan. Nonetheless, as part of the assessment, the panel as a whole travels to Japan to spend at least one week visiting research and development sites and meeting with researchers. These trips have proven to be highly informative, and the panelists have been given broad access to both researchers and facilities. Upon completion of its trip, the panel conducts a one-day workshop to present its findings. Following the workshop, the panel completes its written report.

Study results are widely distributed. Representatives of Japan and members of the media are invited to attend the workshops. Final reports are made available through the National Technical Information Service (NTIS). Further publication of results is encouraged in the professional society journals and magazines. Articles derived from earlier JTEC studies have appeared in *Science, IEEE Spectrum, Wall Street Journal, New York Times*, and others. Additional distribution media, including videotapes, are being tested.

Over the years, the assessment reports have provided input into the policy making process of many agencies and organizations. Many of the reports are used by foreign governments and corporations. Indeed, the Japanese have used JTEC reports to their advantage, as the reports provide an independent assessment attesting to the quality of Japan's research.

The methodology developed and applied to the study of research and development in Japan has now been shown to be equally relevant to Europe and to other leading industrial nations. In general, the United States can benefit from a better understanding of cutting-edge research that is being conducted outside its borders. Improved awareness of international developments can significantly enhance the scope and effectiveness of international collaboration and thus benefit all our international partners in joint research and development efforts.

Paul J. Herer
National Science Foundation
Washington, D.C.

TABLE OF CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

List of Figures

List of Tables

EXECUTIVE SUMMARY

BACKGROUND

The objective of this study was to survey technological activity in separations in Japan, and to compare this activity with that in the United States. For this purpose, the six-person panel and accompanying support personnel spent a week in Japan, visiting one or more sites at seven corporations, five government laboratories, and six universities.

This report describing our findings is organized as follows:

1. this Executive Summary;

2. an introduction and analysis of major issues (Chapter 1);

3. individual chapters delving into particular areas of separations -- separation and purification of gases, water purification, separations of several other sorts involving liquids, hydrometallurgical separations, ion-exchange membrane technology, dewatering and crystallization (Chapters 2-7); and

4. descriptions of the panel's various site visits (Appendices B-F).

A succinct presentation of the JTEC panel's conclusions regarding the relative status and trends of Japanese and U.S. technology and support structure is given in Table E.1. Japan is strong and highly competitive in several areas of separations. For the most part, this position has not been achieved by invention or creative new departures. Instead, it comes from careful selection of the most effective technology available on the world market, followed by diligent implementation, evolutionary advances, strong emphasis on management and control of quality, and effective use of corporate experience. This thrust has been greatly aided by the fact that Japan until recently, in contrast with the United States, has had a steadily expanding economy and growing production, which have provided the opportunity for installation of new capacity with the latest technology.

RELATIVE STATUS AND VECTORS

Table E.1 is the JTEC panel's effort to categorize the relative strengths of separations technology in Japan and the United States. The table is divided into various methods of separation, and also by categories of research, development and implementation for each method. Entries of +, 0 and - refer to the present status of each technology. Entries of ↑, → and ↓ refer to the vector of the comparison, that is,

PRECEDING PAGE BLANK NOT FILMED

PAGE viii INTENTIONALLY BLANK

whether the technology in Japan is gaining, staying about the same, or falling relative to U.S. technology. Following the entries for various methods of separation, the panel addresses certain cross-cutting aspects of research, development and implementation (Table E.2).

Table E.1
U.S. - Japan Comparison by Types of Separation

TOPIC	RESEARCH		DEVELOPMENT		IMPLEMENTATION	
	status	trends	status	trends	status	trends
Gas Separations	-	⇓	-	⇓	-	⇓
Hydrometallurgical Separations	0	⇒	+	⇑	+	⇑
Adsorption	-	⇓	-	⇒	-	⇓
Ultrapure Water	+	⇑	+	⇑	0	⇑
Reverse Osmosis & Ultrafiltration	-	⇑	0	⇒	0	⇒
Ion Exchange Membrane Processes	0	⇒	0	⇑	-	⇒
Membrane Separations of Organics	-	⇒	0	⇒	-	⇓
Extraction						
Solvent	-	⇒	0	⇓	0	⇓
Ion Exchanging	0	⇒	0	⇓	0	⇓
Supercritical Fluid	-	⇒	0	⇑	0	⇒
Crystallization	-	⇒	0	⇑	0	⇒

Legend:

+	Japan ahead	⇑	Japan gaining
0	Japan and U.S. even	⇒	Gap not changing
-	U.S. ahead	⇓	U.S. gaining

Table E.2
General Aspects

	status	trend
Creative Approaches	-	⇓
Development of Existing Approaches	+	⇒
Quality Control	+	⇑
Support of Academic Research	-	⇒
Support of Industrial R&D[1]		⇑
Instrumentation Support	+	⇒
Relevance of University Research	-	⇓
University/Industry Synergy	-	⇓
University/Government Synergy	-	⇒
Government/Industry Synergy	+	⇒

DISTINCTIVE CHARACTERISTICS OF JAPANESE SITUATION

The panel observed a number of distinctive characteristics of the Japanese situation (Chapter 1). Since it has essentially no indigenous energy resources, Japan seeks avenues toward energy independence. Energy costs are high, and there is a strong drive for energy conservation. Energy costs and restricted land area both promote reuse and recycling. In many other areas Japan seeks self-sufficiency; production of salt (NaCl) is an example. Cultural viewpoints and the peculiar nature of the Japanese labor market sometimes bring about specialized approaches. Thrusts in

[1] Note: The panel did not gather sufficient information to rate the current status of support for industrial R&D in Japan compared to that in the United States.

separations technology often support areas of Japanese industrial strength, notably in the electronics industry. Conversely, approaches to meeting separations needs often utilize Japanese strengths, such as instrumentation and photovoltaic technology.

The drive for energy conservation has been particularly apparent in the Japanese paper industry, as is presented and analyzed in more detail in Chapter 7. Environmental concerns are ascendant in Japan, and much is happening in the area of pollution abatement. However, the issue appears to be addressed much less through formal legal regulation, and more through government coordination and influence upon industry, than is the case in the United States.

Universities

Japanese universities utilize the "*koza*" system, where for a particular area a professor is assisted by junior faculty members. This structure enables organized and efficient usage of resources, but would seemingly suppress the development of junior faculty as independent investigators. Research in Japanese universities focuses on derivative advances and supporting information, more than upon creativity and progress toward new scientific understanding. Research facilities in Japanese universities tend to be in very poor condition and crowded. There are major problems of safety and housekeeping, in comparison with the norm in U.S. universities. Research instrumentation is abundant and strong.

Corporations

Corporate activity seems to be relatively more diversified in Japan than in the United States. An example is Kobe Steel, Ltd., which has followed a thread of high-pressure technology that has led the company into a number of very different areas of application.

NATIONAL THRUSTS

Membrane Separations

Japan has national technological thrusts, involving government, industry, government laboratories, and universities. The thrusts most closely connected with separations have been the Aqua Renaissance Project (Appendix G), which deals with water purification, and Project Sunshine and Project Moonlight, which deal with energy independence and related issues. Membrane technologies have been emphasized in these thrusts.

Many of the membrane-based separations activities in Japan have come about through these national initiatives. Membrane separation is an area of Japanese strength, where Japan has about 25 percent of the world market. Membranes are far more prominent among the mix of separation technologies in Japan than in the rest of the world. Here again the Japanese position is not attained through entirely new approaches, but through perceptive selection of available technology, evolutionary improvements, and emphasis upon quality.

The emphasis upon membrane separation technologies in Japan seems to result in large measure from definition of priorities at the government level. The panel can only surmise about the reasons for choosing this emphasis. Synthetic membranes are an area where Japan is already successful and derives considerable economic benefit. Membrane separation may also be regarded as an area where the most opportunities are available for advances. In that sense, the Japanese may regard membrane separations as a less mature technology than do the United States and the rest of the world. Membrane technologies do serve the needs of the strong Japanese electronics industry. For example, membranes are useful in ultrapurification of water (Chapter 3); however, this is an area where U.S. companies (e.g., Millipore) have most of the market. Membrane separations may be regarded in Japan as an effective path for energy conservation and/or technological independence. Developments in membrane technology can lead to advances in technology for batteries, analytical instrumentations and medical applications, notably diagnostics.

Global Environment

Another interesting national thrust pertains to global environmental issues, notably global warming and depletion of the stratospheric ozone layer. Japan has proposed an international plan called "The New Earth 21 (Action Plan for the 21st Century)." The large, main research facility for the Research Institute of Innovative Technology for the Earth (RITE) will be completed in the Kansai Science City in the summer of 1993. One of the areas being given the most emphasis in this initiative is fixation and utilization technology for carbon dioxide (CO_2). As typically described, this involves use of membrane separations to remove and recover CO_2 from the flue gases of fossil-fuel power plants, with conversion of the recovered carbon dioxide to large-scale chemical products such as methanol. This endeavor raises several very fundamental issues concerning feasibility: (1) the very large volume of CO_2 that would have to be recovered to make a difference in the global environment; (2) whether a CO_2-benign source of hydrogen for conversion to chemicals can be achieved; and, (3) whether the uses of recovered CO_2 would themselves return CO_2 to the atmosphere. Therefore the true economic basis for the New Earth 21 initiative is questionable.

SPECIFIC R&D COMPARISONS

Separation and Purification of Gases

Japanese development of technology in gas separations has in general trailed that in other parts of the world, but the commercialized technology in a number of cases may be roughly equivalent to that found elsewhere (Chapter 2). Membrane technology for large-scale, selective recovery of carbon dioxide is receiving attention in connection with the RITE global-warming initiative. However, there is surprisingly little research on membrane technology for other gas separations, especially when the overall Japanese emphasis on membrane separations technology is taken into account. Several small-scale, specialized applications are being developed in connection with the needs of the electronics industry.

Water Purification

Membrane technology for water purification in Japan is largely conventional, but two applications are pushing the limits of current technology -- water for the nuclear industry and water for the production of microelectronic chips (Chapter 3). Approximately 1,000 liters of ultrapurified water are used per wafer in the chip manufacturing industry. The purity required is related to the minuscule dimensions of features on the chips. Contaminants of concern include bacteria, particles, organic matter and dissolved oxygen. Highly sequential purification trains are utilized, with extensive and repeated use of membrane separations and ion exchange. Interestingly, the needs of the Japanese electronics industry are met by vendors of pre-packaged water-purification assemblies, while in the U.S. the tendency is for individual chip manufacturers to assemble their own water-purification plants. The two approaches seem to achieve roughly equivalent results. The water-purification needs for next- and future-generation chips require substantial advances beyond current technology.

Also related to water purification, but on a larger and coarser scale, the panel found that there has apparently been a decision in Japan to replace chlorine with ozone for municipal water treatment. The use of ozone is generally considered to be more expensive and less proven for general use, but it does avoid the formation of trace levels of chlorinated organics.

Separations with Liquids

Much of the research and development activity in Japan for other separations involving liquids focuses on membranes (Chapter 4). Pervaporation, a method of vaporizing a liquid mixture selectively through a membrane, is receiving attention for ethanol-water separation, as it is elsewhere in the world. There is also attention to use of this technique for separation of isopropanol and water (an electronics industry need) and for separations of trace organics from water. There is also work on absorption of nitrogen and sulfur oxides (NO_x and SO_x) from power-plant flue gases and on supercritical fluid extraction, largely for oils and other substances that serve specific Japanese food and flavor needs. Finally, there are several efforts directed toward "chiral" separations, that is, separations of mixtures of optically active isomers.

Hydrometallurgical Separations

There are numerous instances of metals refining and separations in Japan, with substantial and diverse accompanying research (Chapter 5). Emphasis is on smelting and refining, rather than recovery from the ore, since Japan imports most of its metals as concentrates. As in other areas, processes are based upon conventional technology, but a high degree of improvement has been achieved. Equipment is more modern than in the U.S. because Japanese industry has been able to add substantial capacity in recent years. Over the past four decades there has been a major decline in U.S. zinc production. Meanwhile, Japan has become the world's third largest producer of zinc.

There has been a significant amount of research on the fundamentals of leaching, solvent extraction, ion exchange, and chemical and electrochemical reduction. University research in this field is generally of high quality but mainly theoretical.

Ion-Exchange Membrane Technology

Japan has over forty years of experience in the development and manufacture of ion-exchange membranes; much of the development has evolved in the context of producing salt from seawater by means of electrodialysis (Chapter 6). Japan is a world leader in this area, with a broad spectrum of membranes for sale and internal use, with a main theme of environmental applications. Advances are being made in spacer materials and adhesives for membrane modules. Other innovations are in implementation of ion-exchange membranes in tubular geometries (ED CORE, Tokuyama Soda -- see Chapter 6), replacing the conventional flat-sheet geometry, and in bipolar, "water-splitting" membrane technology.

Dewatering (Pulp and Paper Industry)

Japan ranks second and third in world production of paper and pulp, respectively, behind the U.S. in both cases. Over the past two decades Japan has achieved very large reductions in the amount of purchased energy needed for the paper industry -- about a factor of two for the industry as a whole (Chapter 7). For the most part, these savings have not resulted from innovative technology, although the addition of new capacity utilizing newer and more efficient technology has been one factor. Other factors include extensive use of recycle, obtaining a higher concentration of black liquid (separations) within the plants, use of high-pressure and therefore high-temperature boilers, and conversion to continuous digesters.

Crystallization

The most striking technological innovation that the panel found was Kobe Steel's pressure-driven crystallizer, used for separations of organics (Chapter 7). This advance follows from Kobe's practice over the years of using its high-pressure expertise to branch into different areas of application. Increasing pressure, an instantly transmitted thermodynamic parameter, to a great enough extent can bring about solidification in a controlled way, and subsequent reduction and/or cycling of pressure brings about controlled melting that can cause formation of more perfect, and therefore purer and easily separable crystals.

CHAPTER 1

INTRODUCTION

C. Judson King

INTRODUCTION

Separations of mixtures are widely used in industrial processing. Various estimates of U.S. energy consumption attributable to separations are in the range of 5 percent to 10 percent, with 3 percent to 5 percent for distillation alone (Mix et al. 1978; Humphrey et al. 1991). Separations are also the key to many industrial advances, such as the development of biotechnology, purification of water, control of air pollution, refining of fuels, recovery of resources, isolation of pharmaceutical products, disposal of nuclear wastes, and creation of clean processing conditions for manufacture of electronic components (King et al. 1987). Clearly it is an important area for industrial competitiveness and economic development.

The purpose of this study was to survey technological activity in separations in Japan, and to compare this activity with that in the United States. The six panel members listed in Table 1.1 reflected a diverse range of U.S. separations expertise. In addition to the panel members, several observers accompanied the panel (Table 1.2).

The panel spent the week of June 8-12, 1992 in Japan, visiting the various locations described in the site visit reports (Appendices B-F). Industrial visits included chemical, paper, steel, membrane, and water-purification companies. The panel also visited universities and industrial laboratories.

This report represents the panel's best assessment of Japan's separations technology based on the technology examined and evaluated at the sites the panel visited. Innovative technology may have been missed because panel members were not aware of certain developments and did not visit a particular site, or because the developments were proprietary and therefore not made available.

Table 1.1
JTEC Panel Members

C. Judson King (Chair)	Provost and Professor of Chemical Engineering, University of California, Berkeley, CA
Edward L. Cussler	Professor of Chemical Engineering, University of Minnesota Minneapolis, MN
William Eykamp	Former President, Koch Membrane Systems; Consultant, Arlington, MA
George E. Keller	Senior Corporate Fellow, Union Carbide Chemicals and Plastic Co., S. Charleston, WV
H. Muralidhara	Manager, Process Technology, Central Research, Engineering, Cargill Inc., Minneapolis, MN
Milton E. Wadsworth	Professor of Metallurgical Engineering University of Utah, Salt Lake City, UT

GENERAL ISSUES

Unique Characteristics of the Japanese Situation

Certain characteristics of the situation in Japan strongly influence the choice and implementation of separations technology:

1. Japan has no indigenous energy resources, except for some coal. There is a stronger concern with promoting energy independence than is presently the case in the United States. The same is true with regard to resource bases for the manufacture of chemicals.

Table 1.2
JTEC Panel Observers

Bob Williams	Assistant Director, JTEC Loyola College, Baltimore, MD
David Roswell	Dean, College of Arts and Sciences Loyola College, Baltimore, MD
Henry McGee, Jr.	Division Director for Chemical and Thermal Systems, National Science Foundation, Washington, D.C.
Gene Lim	Advance Contractor, JTEC Murrysville, PA

2. For similar reasons, energy costs are relatively high in Japan. There is consequently a strong drive for energy conservation. The reductions of energy consumption achieved over the last fifteen years in the Japanese paper industry are truly impressive (see Chapter 7).

3. Japanese policymakers often view issues from the standpoint of self-sufficiency. An example is the development of technology for the manufacture of salt. Using the sea as its resource, Japan has developed a unique electrodialysis process that recognizes Japan's relative lack of available coastal land area for solar evaporation ponds, and provides Japan with a unique technology base. Governmental subsidies are made available to promote self-supporting technology.

4. Japan often views things from a cultural viewpoint to a greater extent than is the case in the United States.

5. Processing approaches adopted in Japan can be labor-intensive. Assembly of plate-and-frame membrane equipment is one example.

6. Developments in separations technology support areas of industrial strength. The strength of the electronics industry relative to the chemical industry is greater in Japan than in the United States. Hence the development and implementation of separations technology in Japan serves the electronics industry to a greater extent than is the case in the United States. That is where the greater financial gains are available to the vendors of technology. Examples are the production of ultrapure water and clean-room technology.

7. The restricted land area in Japan promotes the concept of recycle and reuse. A significant amount of separations technology stems from this incentive.

8. Over the past one to two decades, Japan has been able to introduce new technology because of the need to add capacity in an expanding economy. Examples are metals processing (Chapter 5) and paper manufacture (Chapter 7). The technology added has usually not been Japanese, but new capacity has given the Japanese the opportunity to bring it into practice more rapidly than in countries without such economic growth.

9. The relative strength of Japan's electronics industry leads to favoring approaches to separations and separations research that trade upon that strength. Thus there is strong interest in energy distribution in the form of stored hydrogen (e.g., metal hydrides), using photovoltaics for water electrolysis. There is also heavy use of sophisticated instrumentation in support of research and development.

10. Finally, there are national technological thrusts in Japan, coordinated by the Ministry of International Trade and Industry (MITI) working in coordination with industry. Aqua Renaissance, a now completed initiative, dealt with various aspects of water purification, with emphasis upon membrane separation technology (see Appendix G). Project Sunshine, a completed thrust, and Project Moonlight deal with energy independence and conservation. Both of these have included research and developments pertaining to membrane separations, among many other areas. Finally the new New Earth 21 initiative, which deals with global environmental initiatives, includes a separations component. Instead of being designed and coordinated from above, New Earth 21 appears to consist of a number of diverse activities at different locations, with each participating institution conceiving and selecting what it feels it is best able to do in contributing to the overall goal.

General Characteristics of Japanese Separations Technology

As a rule, separations technology in Japan emphasizes effective implementation rather than innovation. Only rarely does one find a major, creative new departure. Instead, the tendency is to use proven, existing technology, with evolutionary improvements. The approach is to carry out the implementation of these techniques carefully and diligently, with strong emphasis on quality control and effective use of corporate experience.

The Emphasis on Membranes

Research in Japan on separations technology is heavily concentrated toward various membrane separations. Industrial research is supported by research in government laboratories. There have been two national research initiatives (Aqua Renaissance '90 and Project Sunshine) in which membrane research has been an important component, and another (Project Moonlight) is presently underway (Japan Technical Information Service).

Japan currently produces 20 percent to 25 percent of the world's supply of membranes, worth about $400 million (King 1988). In order of size, the top five producers of membranes in Japan are Asahi Chemical Industry Ltd., Toray Industries, Inc., Teijin Ltd., Asahi Glass Co., Ltd. and Kuraray Co., Ltd. The panel visited Toray, Asahi Kasei, Nitto Denko, Tokuyama Soda and Kurita Water Industries.

The panel can only surmise why membrane separations technology has been chosen for so much emphasis. It is, of course, an area where Japan is already successful and derives substantial economic benefit. It may also be regarded in Japan as the area where the most opportunities are available for advances. In this sense, it may be perceived as a less mature technology than it is in the United States. Membrane separations do support the needs of the electronics industry, a Japanese strength; however, it appears that U.S. companies (e.g., Millipore) still have most of the market for supplying membranes to the Japanese electronics industry. Membrane separations may also be regarded as a good path for energy conservation and/or as a road toward technological independence.

There may be future technological developments deriving from Japan's chosen emphasis upon membrane technology. One could be leadership in the area of battery technology, which trades upon ion-exchange membranes. Another could be technology for medical applications, notably diagnostics.

Japanese Universities

The Japanese universities are based on the "*koza*" structure, where for any one area there is a senior professor, typically assisted by an associate professor and one or more assistant professors and/or instructors. The research of this group focuses on collective interests, with the research chosen by the professor.

There are certain natural results of this structure. One is that there seems to be little or no opportunity for independent scientific development of the associate and assistant professors, as opposed to the situation in most U.S. universities. Nonetheless, the associate professors whom the panel met did seem to be technically strong.

In comparison with the United States, research in separations in Japanese universities trades less upon creativity and progress towards new scientific understanding. Instead, Japanese research makes derivative advances and provides supporting information. There are, of course, significant exceptions.

The panel noticed that research facilities in Japanese universities tend to be cramped and in very poor condition, with major problems of safety and housekeeping. Fume hoods (known as "drafters" in Japan) are inadequate and sometimes missing altogether in laboratory rooms where they are much needed. It appears that accidents are often waiting to happen. Needs range from more space to upgraded space to new buildings.

By contrast, most of the areas of the universities that the panel visited have good scientific instrumentation. In several instances the instrumentation is superior to what exists in U.S. universities, for example, 300-mHz NMR (nuclear magnetic resonance), FT-IR (Fourier transform infrared spectroscopy), ESR (electron spin resonance) and GC-MS (gas chromatography coupled with mass spectrometry) in individual research groups.

Government/Industry/University Interactions

Figure 1.1 shows the development structure in Japan for alternative energy technologies, i.e., alternatives to petroleum (King 1988). The very substantial roles of government subsidy and the potentially important role of support from government laboratories are apparent. Government subsidies are applied to support identified key areas (e.g., membrane technology), and the national laboratories seek to carry out supporting fundamental research. From the panel's limited investigations, it seems that the supporting role of government laboratories is not yet highly effective.

Government Laboratories

Since 1963 the Japanese government has had a policy of concentrating government laboratories in the science city at Tsukuba. The mission of these laboratories seems to be defined as the conduct of fundamental research in support of industrial and government priorities. The centralized location obviously helps interaction among the laboratories; however, there seem still to be complications resulting from the divided administrative structure. For example, membrane research was present at several different laboratories, but it was not apparent how (or whether) it is decided which laboratories should work on which areas of membrane technology. We understand that as of January 1, 1993 a new National Institute of Materials and Chemical Research was created by combining several of these laboratories.

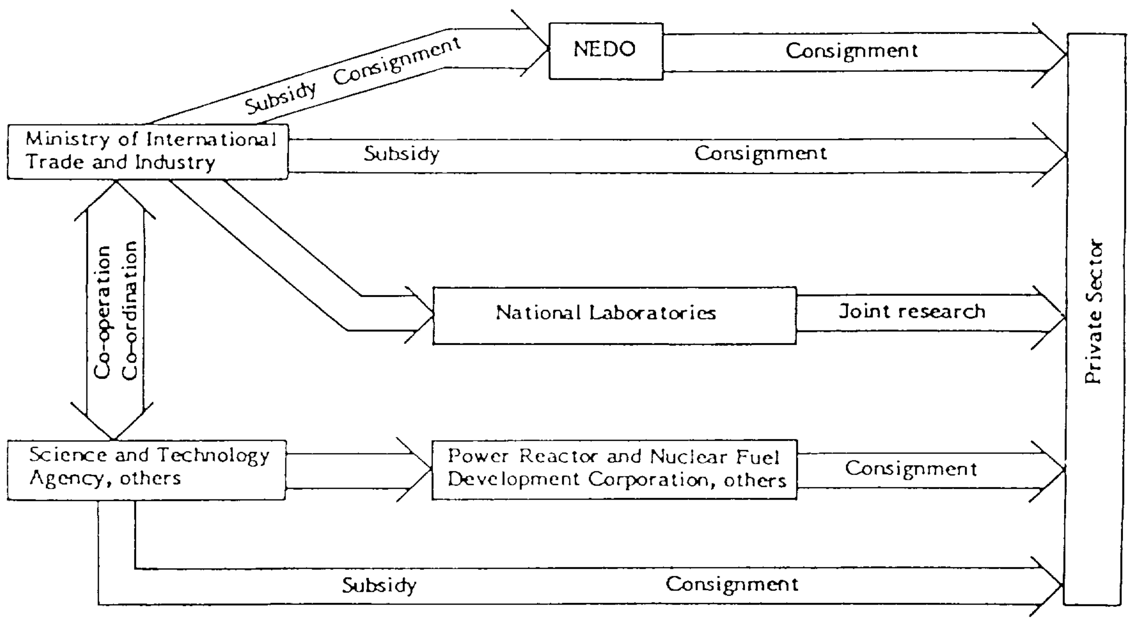


Figure 1.1. Japan's Development Structure for Oil-alternative Energy Technologies

In the United States, the government laboratory that seems closest in mission to the MITI laboratories is the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards. In comparison, NIST seeks to play more of a leading role in devising generic technology for industrial use, and has recently developed a technology transfer function. Government laboratories in Japan seem more directly responsive to stated needs of Japanese industry.

The facilities in the government laboratories are far superior to those in universities and are close in quality to those in industry. There does, however, appear to be a substantial lack of technicians, shops and other support services.

Diversification of Corporate Technology

Corporate activity tends to be diversified in Japan, perhaps in part because new and diverse ventures serve to keep the employees well deployed.

An example is Kobe Steel, Ltd. Kobe Steel has undertaken a number of diversifying activities of a sort not pursued by steel companies in the United States. For example, Kobe Steel has activities in high-pressure crystallization of organics from the melt, preservation and processing of foods through application of high pressure, supercritical fluid extraction, and liquefaction (hydrogenation) of Australian brown coal. The latter effort is encouraged and subsidized by the Japanese government. Kobe Steel's activity in supercritical fluid extraction is also subsidized by the government. This diversification seems to result from a search for ways to utilize accumulated expertise in high-pressure technology (see Fig. 1.2).

Energy Conservation

Energy conservation has been a priority in Japan because of the lack of indigenous energy resources and the high cost of energy.

The panel received a graphic analysis of energy conservation in the Japanese paper industry from Jujo Paper Central Research, reported in Chapter 7. Purchased energy for the paper industry in 1990 had been reduced to 50 percent of what it was in 1975, the high year. It was pointed out that at Jujo Paper, and probably for the industry as a whole, energy conservation has been company policy for about twenty years. Because of this, many proposals for ways of saving energy come forward from the working level. The company *asks* its operators to make such proposals.

Pollution Abatement

It is apparent that environmentalism is sharply on the rise in Japan and is increasing industrial attention to reducing potentially harmful or disagreeable effluents. Since recovery, recycle and reuse are alternatives to degradation processes for effluent treatment, this trend has major implications for the use of separations technology. Although practices are changing rapidly, it appears that Japanese industry has not reached the degree of effluent control characteristic of U.S. industry.

One example is control of dioxin in effluents from the paper industry. There is public concern and political pressure on this issue, but there is as yet no legislation. The Japanese Environmental Protection Agency continually samples seawater near coastal paper plants and has concluded that dioxin levels are not hazardous.

At the Jujo Ishinomaki plant, the chemical oxygen demand (COD) of water and the SO_x and NO_x contents of exhaust air are monitored.

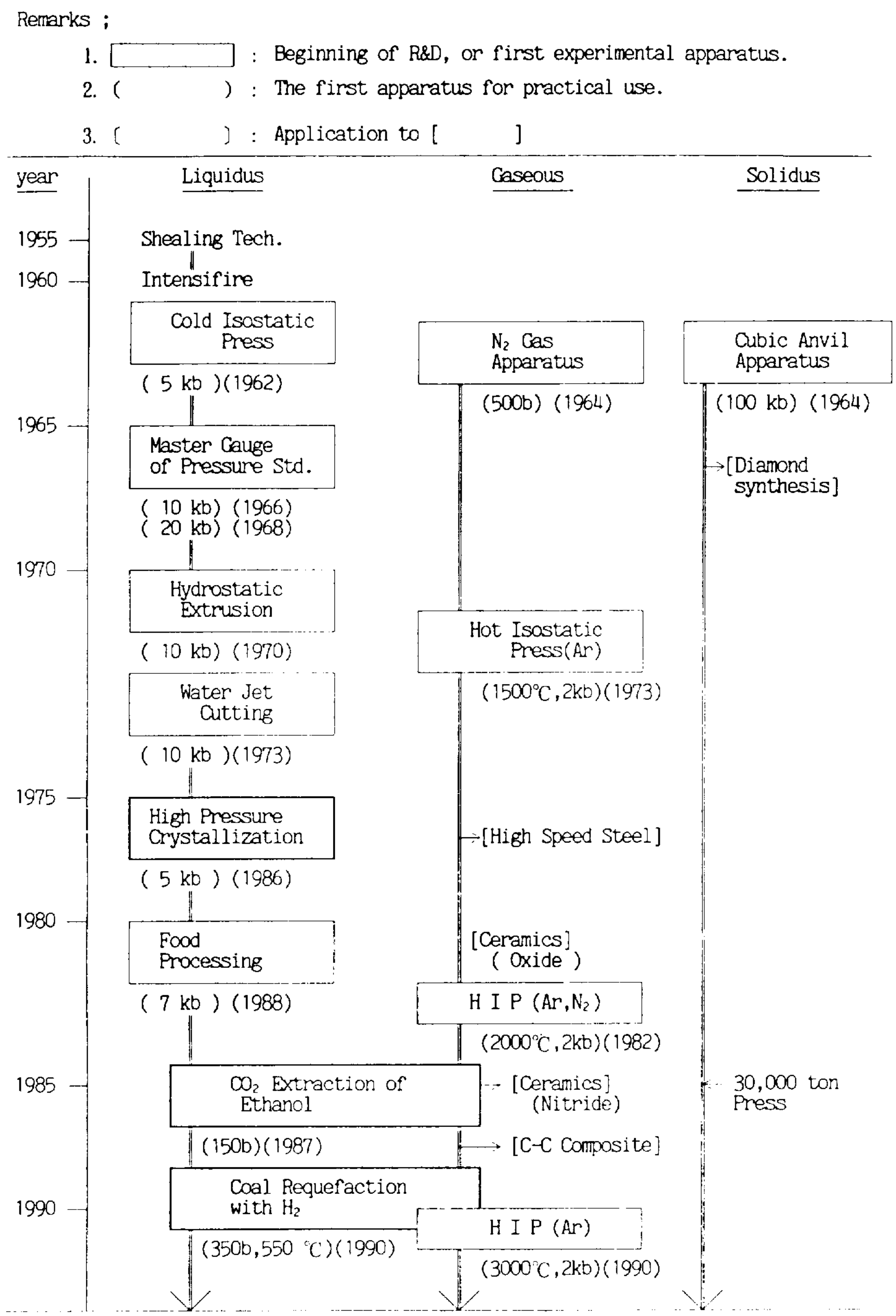


Figure 1.2. Developments of High Pressure Technology (Kobe Steel)

Global Warming

Japan has set up a new initiative pertaining to global environmental issues. The New Energy and Industrial Technology Development Organization (NEDO) launched research and development activities in this area in 1990, subsidized by MITI. One means of implementation is the Research Institute of Innovative Technology for the Earth (RITE). The main research facility, which will be in the Kansai Science City, is scheduled for completion in the summer of 1993. Japan has proposed an international plan called The New Earth 21 (Action Program for the 21st Century). RITE is intended to serve as a hub of that effort.

Components of The New Earth 21 are shown in Figure 1.3. Separations pertain to several of these elements, but the one relating most closely to this study is number 3, development of environment-friendly technology, which includes, *inter alia*, fixation and utilization technology for carbon dioxide. The panel encountered several locations where research is being carried out on means of recovering carbon dioxide from gases, for example, flue gases from fossil-fuel power plants. At the National Institute for Resources and Environment, research is being carried out postulating large-scale conversion of recovered carbon dioxide to methanol, as discussed in Chapter 2.

Conversion of CO_2 to methanol requires substantial quantities of hydrogen [CO_2 + $3H_2$ -> CH_3OH + H_2]. If this hydrogen comes from a fossil-fuel source, for example, steam reforming of methane [CH_4 + $2H_2O$ -> CO_2 + $4H_2$], there is little gain. However, it may be that Japan is seeking to make hydrogen by electrolytic splitting of water, using solar photovoltaic technology.

Furthermore, the amount of methanol produced by recovering CO_2 from fossil-fuel power plants would be very large, and a use for that methanol would be needed. There may ultimately be a large market for methanol as transportation fuel. This would, of course, return the recovered carbon dioxide to the atmosphere, having been used twice, however.

It is difficult to lessen global CO_2 release significantly by recovering CO_2 from effluent gases, as opposed to lessening releases through energy conservation, switching energy and resource bases, etc.

ACKNOWLEDGEMENTS

The panel appreciates the support of the JTEC staff. As well, we wish to acknowledge the very considerable support and assistance given by Dr. M. Gene Lim, without whom we would not have been anywhere near as effective. Dr. Henry McGee of the National Science Foundation, Dean David Roswell of Loyola College,

and Bobby Williams of JTEC traveled with us during much of the panel's week in Japan.

Many of our hosts in Japan went far above and beyond the call of duty in accommodating us and facilitating our work. Among many, we particularly acknowledge and thank Dr. Masato Moritoki of Kobe Steel, Kiyoaki Iida of Jujo Paper, Professor Morio Okazaki of Kyoto University, and many others too numerous to name.

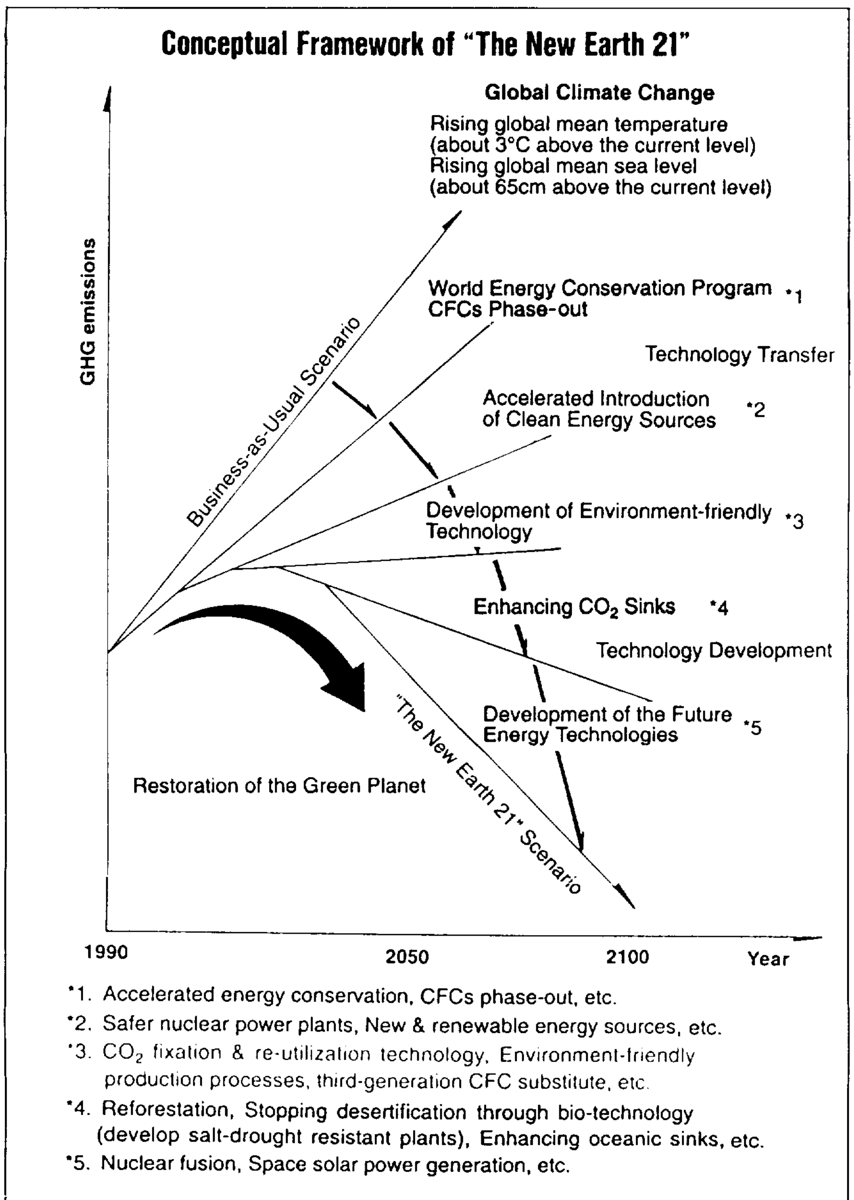


Figure 1.3. Components of "The New Earth 21" (Courtesy, Research Institute of Innovative Technology for the Earth)

REFERENCES

Humphrey, J. L., A. F. Seibert and R. A. Koort. 1991. *Separation Technologies Advances and Priorities.* Report No. DOE/ID/12920-1. U.S. Department of Energy.

Japan Technical Information Service. *Polymeric Membranes in Japan: Technological Development and Commercial Utilization.* Materials Technology in Japan Series. Amsterdam, the Netherlands: Elsevier.

King, C. J., et al. 1987. *Separations and Purification: Critical Needs and Opportunities.* National Research Council, Board on Chemical Science and Technology, National Academy Press.

King, R., ed. 1988. *Modern Japanese Membranes.* BHRA The Fluid Engineering Centre, United Kingdom.

Mix, T. W., J. S. Dweck, M. Weinberg and R. C. Armstrong. 1978. *Chem. Eng. Progress* 74 (4):49.

CHAPTER 2

SEPARATION AND PURIFICATION OF GASES

George E. Keller

INTRODUCTION

Gas-separation processes serve a very wide range of applications, from the very large, e.g., air separation, to the very small, e.g., purification of specialty gases for use in the electronics industry. Typical applications are summarized in Table 2.1. These applications are in turn accomplished by a relatively small number of types of processes, typical examples of which are given in Table 2.2. For a number of separations, several processes may compete with each other, the economically decisive variables usually being the required product purity, production rate, feed composition and feed pressure. Japanese technology development in gas separations has in general trailed that in other parts of the world, but their commercialized technology in a number of cases may be roughly equivalent to that found elsewhere. In several cases there are interesting technological and programmatic developments that bear watching.

AIR SEPARATION

O_2/N_2

The largest-volume air-separation units are based on cryogenic distillation, a technology that has reached a high degree of technological maturity both in Japan and the United States. Smaller-volume units are often based on pressure-swing adsorption (PSA) and membranes, the latter for nitrogen only. PSA units appear to be of conventional design and to use conventional zeolite molecular sieves. Sumitomo Seika has sold PSA units for oxygen production up to about 150 tons per day. Other companies such as Seitetsu Kagaku and Kobe Steel also offer PSA technology for oxygen production. PSA processes for nitrogen production appear to be based, for the most part, on German technology, using carbon molecular sieves from Bergbau Forschung GmbH. Except for isolated research projects, the panel could uncover no indication that much effort was being expended on improving the adsorbents for air-separation PSA processes. The most interesting work on adsorbents was at Kyoto University's Department of Chemical Engineering, where researchers have found a way to produce carbon molecular sieve structures with adjustable-diameter, narrow-pore-size-distribution pores. Such structures may provide a new series of adsorbents, based on intra-particle diffusion rate selectivity, for air separation and other important separations.

Table 2.1
Examples of Commercial Gas Separations

Air separation for recovery of oxygen, nitrogen and argon
Separation and purification of rare gases
Removal of ethane and higher hydrocarbons from natural gas
Hydrogen recovery and purification
Synthesis gas (carbon monoxide/hydrogen) ratio adjustment
Separation and purification of light hydrocarbon gases such as methane, ethane, ethylene, acetylene, propane, propylene, etc.
Removal of water vapor from gases
Removal of acidic gases such as hydrogen sulfide, carbon dioxide, sulfur oxides, hydrogen chloride, etc., from gas streams
Recovery of ammonia from gas streams
Recovery of carbon monoxide
Removal of small concentrations of organic and inorganic contaminants from off-gas and chemical-process streams

The paucity of written and oral references to membrane-based processes for air separation suggests that the commercial use of this technology has not progressed to the point that it has in the United States.

Air/Water

There appears to be some interest in air drying. For example, Ube Industries is investigating polyimide membranes for selective permeation of water. There is no indication that this effort and other efforts in Japan have produced membrane performances that rival those found in the United States.

Table 2.2
Examples of Processes Used in Commercial Gas Separations

PROCESS	TYPICAL USES
Distillation	Air separation, hydrogen recovery and purification, synthesis gas ratio adjustment, separation and purification of light hydrocarbon gases, recovery and purification of rare gases
Absorption	Gas drying; removal of hydrogen sulfide, carbon dioxide and sulfur oxides, etc., from flue gases and other streams; carbon monoxide recovery, ammonia recovery
Adsorption	Air separation, hydrogen recovery, synthesis gas ratio adjustment, gas drying, removal of various organic and inorganic contaminants from air and process gas streams
Membranes	Nitrogen production from air, hydrogen recovery, removal of organic vapors from vent streams, carbon dioxide recovery from enhanced-oil-recovery operations

OTHER LARGE-VOLUME GAS SEPARATIONS

Hydrogen

In general, the pattern of commercial hydrogen recovery and purification in Japan appears to track that in the United States. Many large units are cryogenic-based, but PSA units are also in use. These latter units are based both on Bergbau

Forschung carbon molecular sieves as well as on zeolite molecular sieves. Large-scale production of very-high-purity (99.999 percent) hydrogen via PSA is commercially established. The commercial practice of membrane-based hydrogen upgrading may lag that in the United States. There is no indication of breakthrough technologies in hydrogen recovery and purification in Japan.

CO_2

A major program is underway in Japan to deal with the problem of buildup of carbon dioxide in the earth's atmosphere, which is the dominant factor in the so-called greenhouse effect. The New Energy and Industrial Technology Development Organization (NEDO) launched research and development activities in this area in 1990, subsidized by the Ministry of International Trade and Industry. A major organization in this program is the Research Institute of Innovative Technology for the Earth, located in Kansai Science City. Among the thrusts of the program is biologically-based and chemically-based carbon dioxide fixation. The sources of carbon dioxide will be stack gases from stationary power plants (see Fig. 2.1). The chemically-based system is projected to consist of a membrane unit to produce a concentrated stream of carbon dioxide from the stack gas. The carbon dioxide will be subsequently reacted with hydrogen to produce useful chemicals and fuels. As a result of this thrust, research on improved membranes for carbon dioxide permeation appears to be heating up at the University of Tokyo and other laboratories. The objective is to produce simultaneous increases in carbon dioxide permeability and selectivity.

A potential problem is how the hydrogen will be produced. If it is produced from a fossil fuel, then the net reduction in carbon dioxide generation will be negligible. Thus non-fossil-fuel-based ways of producing hydrogen must be incorporated into the process. Water splitting, using solar energy, is one scenario being investigated. However, since investments are likely to be very large for this scenario, it is too early to tell what impact the NEDO program will ultimately have.

A vacuum PSA process has also been developed and commercialized by Sumitomo Seika on large scale (3,000 normal m^3/hr) for carbon dioxide removal from stack gas. In addition, more or less standard absorption processes based on ethanolamines and other solvents are in use for higher-than-atmospheric-pressure streams.

CO

Carbon monoxide recovery from low- and high-pressure streams has received substantial attention. Cryogenic recovery is common. The COSORB process, licensed from Tenneco in the United States, is also used. This process uses cuprous chloride dissolved in a hydrocarbon solvent to absorb carbon monoxide selectively. Kobe Steel, Ltd. and the Kansai Coke and Chemicals Co. have developed a special carbon monoxide-selective adsorbent consisting of cuprous chloride on activated alumina. This process has been in commercial operation since 1989. The correct choice of process depends on plant capacity, the required carbon monoxide purity, the feed gas composition and pressure. Studies at Kyoto University's Department of Chemical Engineering have been made on impregnating activated carbon with various metals and metal salts. So far, this work does not seem to have uncovered commercially productive leads.

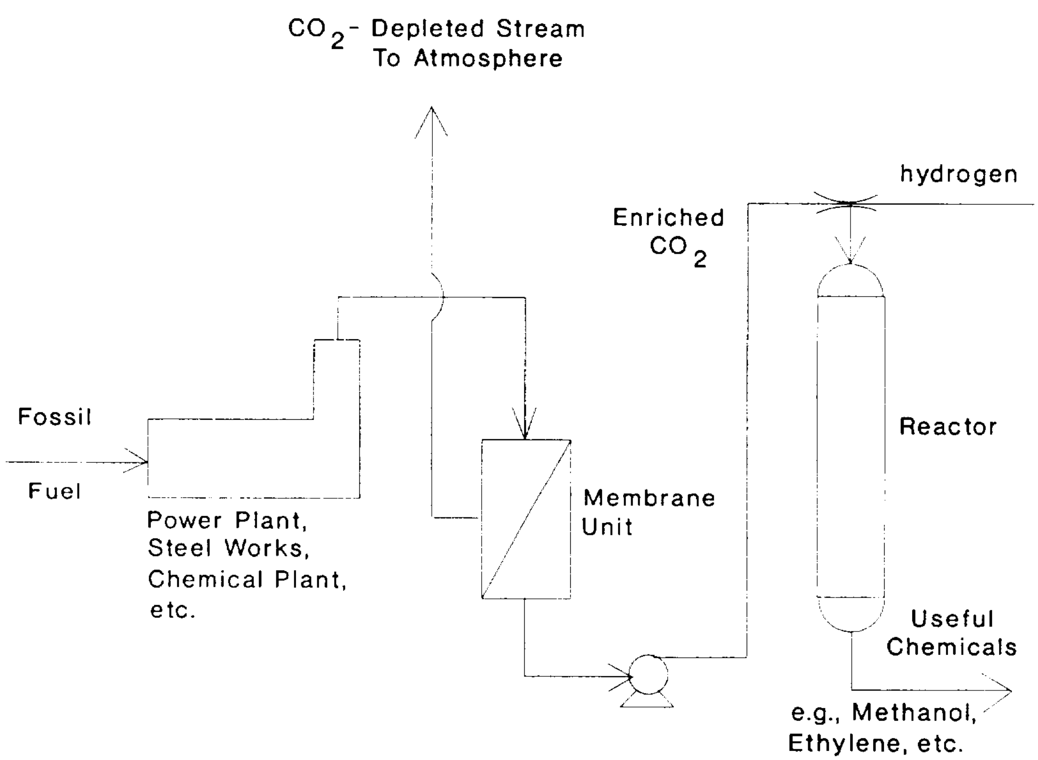


Figure 2.1. Proposed Scheme for Reduction of CO_2 Emissions: Chemically-Based CO_2 Fixation

Argon

The recovery of argon via vacuum PSA from various gas streams from steel mills and other sources has been commercialized. This process requires that the feed stream contain virtually no oxygen, since oxygen has adsorption characteristics similar to argon.

Flue-Gas Desulfurization

The removal of sulfur oxides (SO_x) and nitrogen oxides (NO_x) from stack gases is of real concern in Japan and appears to be a continuing focus for research and development. For example, in 1976 Kobe Steel developed and commercialized a process based on absorption of SO_x into an aqueous calcium chloride solution containing lime ($Ca(OH)_2$). In reacting with SO_x, the lime is converted to calcium sulfite and sulfate, and eventually into all sulfate (gypsum). This process is available for licensing. Other companies are also undoubtedly working on SO_x removal via absorption. There may be some membrane-based research also. Most of the approaches for removal of NO_x are based primarily on reactions that convert it to nitrogen.

SMALL-VOLUME AND SPECIALTY SEPARATIONS

There is a growing number of separations in which flows are considerably smaller than those normally found in large-scale chemical processes. For example, small, PSA-based oxygen generators are offered for sale by Sumitomo Seika. These units, which have flows from 2 to 200 liters per minute, can be used to supply oxygen for ozone processes, metal-cutting operations, health-care applications and other applications. PSA nitrogen generators using carbon molecular sieves and with capacities from 1.5 to 12.6 liters per minute are also sold by the same company. These units have various uses in chemical laboratories and for blanketing and various inert-atmosphere applications.

Another area of process development is the recovery of Freon 113 from air via adsorption. This material is a commonly used solvent for washing semiconductor parts during manufacture, and its release to the atmosphere is unacceptable in light of its tendency to facilitate destruction of ozone in the upper atmosphere. Small units have been developed for sale by Kobe Steel using both temperature swing and vacuum to recover the Freon from the activated carbon adsorbent. The carbon is in the form of a monolith that facilitates very low pressure drops while maintaining effective contacting of gas with adsorbent.

Kobe Steel has also commercialized a small, monolithic, activated-carbon bed for the removal of ozone from air and other gas streams via reaction to oxygen.

It is likely that other Japanese companies are also working on developing monolithic structures containing various adsorbents, and in this area of technology, the Japanese may well be ahead of the United States. For situations involving adsorption at atmospheric and near-atmospheric pressures, pressure drop becomes a primary economic consideration; hence the importance of this technology development.

The electronics industry is also the focus of a series of small-scale processes to purify the various gases, such as silane, arsine, diborane and others, which are used in various steps in the manufacture of chips. Little is known about such purification processes, but it is obvious that a great deal of care must be taken. Other areas for specialty gases include calibration samples for gas mixtures, medical markets, and aerosol propellants. Most of the gases serving these markets are delivered to the customers in cylinders.

As Japanese companies that are in the business of selling separation-process technology look for additional ways to increase the size of their businesses, it is inevitable that they will look carefully at the field of scaled-down processes for specialized uses. Such companies in Japan may be further along in realizing the potential for such businesses than their U.S. counterparts.

CONCLUSIONS

Overall, it appears that Japan's position in gas-separation technology is adequate but not outstanding. The panel was not able to uncover any signs of truly breakthrough gas separations technology, either in the laboratory or commercialized. Many Japanese processes appear to be closely akin technologically to those in the United States, and the U.S. processes were in general commercialized much earlier and are perhaps more advanced. Nevertheless, it appears that Japan's PSA and other processes are licensed aggressively, especially to Far East markets, and Japanese companies that are licensing these processes should be able to compete well against U.S. companies seeking to license similar processes in this part of the globe. Because of Japan's relatively high energy costs, separation processes there are probably designed and optimized for a high-energy-cost environment, which is also characteristic of many other Far East countries. This fact could also help Japanese companies in licensing their processes.

One major conclusion regarding membrane-based separation processes is that the vast fraction of the research, development and commercialization of such processes has been done on liquid separations rather than on gas separations. As opposed to the many and varied commercial applications for membranes in liquid separations, commercial gas-separation applications are extremely limited in Japan. Even at the research stage today, there appears to be only a small amount of applications research, except for carbon dioxide-removal studies.

There are technology developments and technology trends in gas separations in Japan that could be especially significant and possibly ripe for cooperative efforts with U.S. researchers. These include:

1. **New adsorbents and adsorbent geometries**. Research and development in this area does not appear to be extensive for now, but some interesting leads may result. Especially important is the work on monolithic adsorbent structures. If the usual problems of mechanical integrity and cost per unit of adsorbent can be overcome, then this area should blossom in the same way that the market for structured packing has in distillation.

2. **Environmentally-oriented gas separations**. There appears to be a strong desire for improvement of the quality of the environment on the part of the Japanese government, and this desire should translate into more research and development in this area. New processes could result.

3. **Reduction of carbon dioxide emissions to the atmosphere**. This thrust, which is initially aimed at reducing carbon dioxide emissions from stationary power plants and other large sources, is receiving a great deal of attention by the Japanese government. There are many problems to be overcome, including low-cost recovery, concentration and clean-up of carbon dioxide from the stack gas; generation of hydrogen without further generation of carbon dioxide; identifying large enough sinks for the recovered carbon dioxide; and assembling an overall technology package that will be economically attractive. This program should be considered relatively long-range and high-risk, but with the potential to develop a series of new technologies.

4. **Scaled-down separation processes for specialized uses**. The Japanese have been active in this field in the past. Activity in this area will probably increase as new areas are identified and recognized as important.

CHAPTER 3

WATER PURIFICATION

William Eykamp

INTRODUCTION

Pure water has many meanings. Potable water is pure in the sense that there are standards for biological activity and numerous toxic materials. Chemical manufacture generally requires water purer than potable water, specifically regarding ion concentrations. Laboratories use distilled water, now almost always produced by processes other than distillation. Pharmaceutical standards for injectable water are yet more detailed and codified.

For all of these types of purified water, well known techniques may be employed. Innovation focuses on how to produce the requisite water at ever lower cost. Japanese technology for potable water and moderate degrees of further purification is centered on reverse osmosis and ultrafiltration, as in most of the rest of the world. The technology is conventional.

Also related to water purification, but on a larger and coarser scale, the panel found that there has apparently been a decision in Japan to replace chlorine with ozone for municipal water treatment. The use of ozone is generally considered to be more expensive and less proven for general use, but it does avoid the formation of trace levels of chlorinated organics.

In two instances, however, the requirements for high purity water are pushing the limits of separations technology. These are water for the nuclear industry, and water for the production of microelectronic chips.

OBSERVATIONS

The JTEC panel visited several firms having a strong interest in water. The conversations were almost exclusively on water for the electronics industry. This report will focus on water for chips.

News reports chronicle the march towards more sophisticated chips. DRAMS with capacities of 1 megabit (Mb), 4 Mb, and 16 Mb have been developed. Work on the 64-Mb generation is already underway, and an announcement was made in July 1992 of a three- company, three-nation assault on the 256-Mb device.

As the capacity of the chip grows, the width of conduction paths and other features shrink. Feature widths are of the magnitude 0.5 μm for current generation chips, dropping to 0.3 μm on chips under development. Each wafer is exposed to rinse water after most of its many fabrication operations. The rule-of-thumb is that a wafer will see 1,000 liters during its trip through the fabrication line. Because of the volume of water needed to rinse each wafer, and because many impurities favor surfaces, the permissible level of particles, bacteria, ions, and so forth, in water declines inexorably towards zero on a scale where zero cannot be reached.

The importance of water purity may be illustrated by considering several facts. A wafer starts as a silicon metal plane, but as production progresses, it is quickly turned into a three dimensional object, with etched lines, contact holes, through holes, and so forth. Chemical etching does not produce neat rectangular lines; in fact, undercutting is normal. In these cavities, water will remain, and any impurity will concentrate as the water evaporates. Common contaminants in water affect the electronic behavior of silicon. Bacteria are a particular problem, as they are ubiquitous in water. Even after every attempt to remove them, if even a few avoid destruction they will multiply in pipes, ion exchange resins, membrane backings, and elsewhere. All bacteria contain the essential elements C, H, and O, but they also contain N, P, K, Na, Ca, and others. P, for example, is used as a dopant in silicon semiconductors. If a bacterium is left on a wafer, localized P doping may result in a defective chip. Particles adhering to a wafer interfere with lithography, and they can also be significant in size compared to oxide films and other features. Organic matter will decompose during annealing, producing variable oxide layer thickness.

Another complication in the improvement of the process is the absence of non-destructive tests for in-process quality determination, and the absolute minimum of seven days from the beginning of fabrication to the first meaningful test of success.

This long time delay, coupled with the compelling necessity of raising yields, encourages conservatism on all controllable inputs, water clearly among them (Leachman 1992).

Since Japan and the United States are on the cutting edge of microelectronics, the panel was interested in investigating the technology for making ultrapure water in Japan. The panel visited Kurita, the largest supplier of ultrapure water equipment to the semiconductor industry in Japan, and several membrane companies that supply reverse osmosis and ultrafiltration membranes to that industry.

Kurita supplied its flowsheet for ultrapure water, shown in Figure 3.1. Additional information on ultrapure water technology at Toray, Nitto Denko, and Asahi Chemical is provided in Appendix B.

"Preblock," the equivalent of a roughing filter, removes particles, colloids, bacteria, and dissolved macromolecules. Kurita uses proprietary UF spiral elements. Others use conventional coagulation, sedimentation, and filtration. The CO_2 scrubber is a packed tower that uses filtered air as a stripping agent. Next the water is passed through two reverse osmosis units in series. These remove almost all dissolved species. O_2 is then lowered to 5 parts per billion (ppb) by stripping in a packed bed with 99.999 N_2. After a surge tank with N_2 blanket, O_2 is reduced further in a bed packed with ion exchange beads on which Pd has been coated, H_2 being the reductant. The O_2 level at the exit is < 1 ppb. Ion exchange is next, first cation then mixed bed, following a surge tank. Total organic carbon (TOC) is reduced via low pressure UV oxidation to < 2 ppb. Dissociated water is the source of oxygen for the oxidation of organics. (Others may reduce TOC by different means.) The water is then passed through a special super purity mixed bed ion exchange resin and UF to produce specification-grade water.

Table 3.1 gives water specifications for water suitable for 16 Mb chips. This table is a compilation of several sources in Japan for specifications for 16 Mb quality water. Also shown is Kurita's estimate for the next generation. A comparable table supplied by Asahi Chemical is included in the Asahi site report in Appendix B.

Kurita claims that water of the quality given in column 1 of Table 3.1 is available and can be delivered routinely. This assertion is supported by the assurance of a major U.S. testing lab that water samples received from leading chip fabricators in the United States are at the levels cited, save for dissolved O_2 (Balazs 1992).

With regard to the actual water used in fabrications, there seems to be little difference between the water found in the United States and in Japan. Many experts think U.S. water has traditionally been better. What about the future?

The panel found a real difference in the vendor-buyer relationship between the two countries. In Japan, the engineering company, usually Kurita or Japan Organo, possesses the know-how and has access to the equipment to permit it to build and install a high performance system with minimal input from the buyer. U.S. practice is for far more buyer involvement, including specification of some or most of the equipment used to produce the water. The U.S. company is much less likely to purchase a turnkey installation with strict vendor responsibility for the end product.

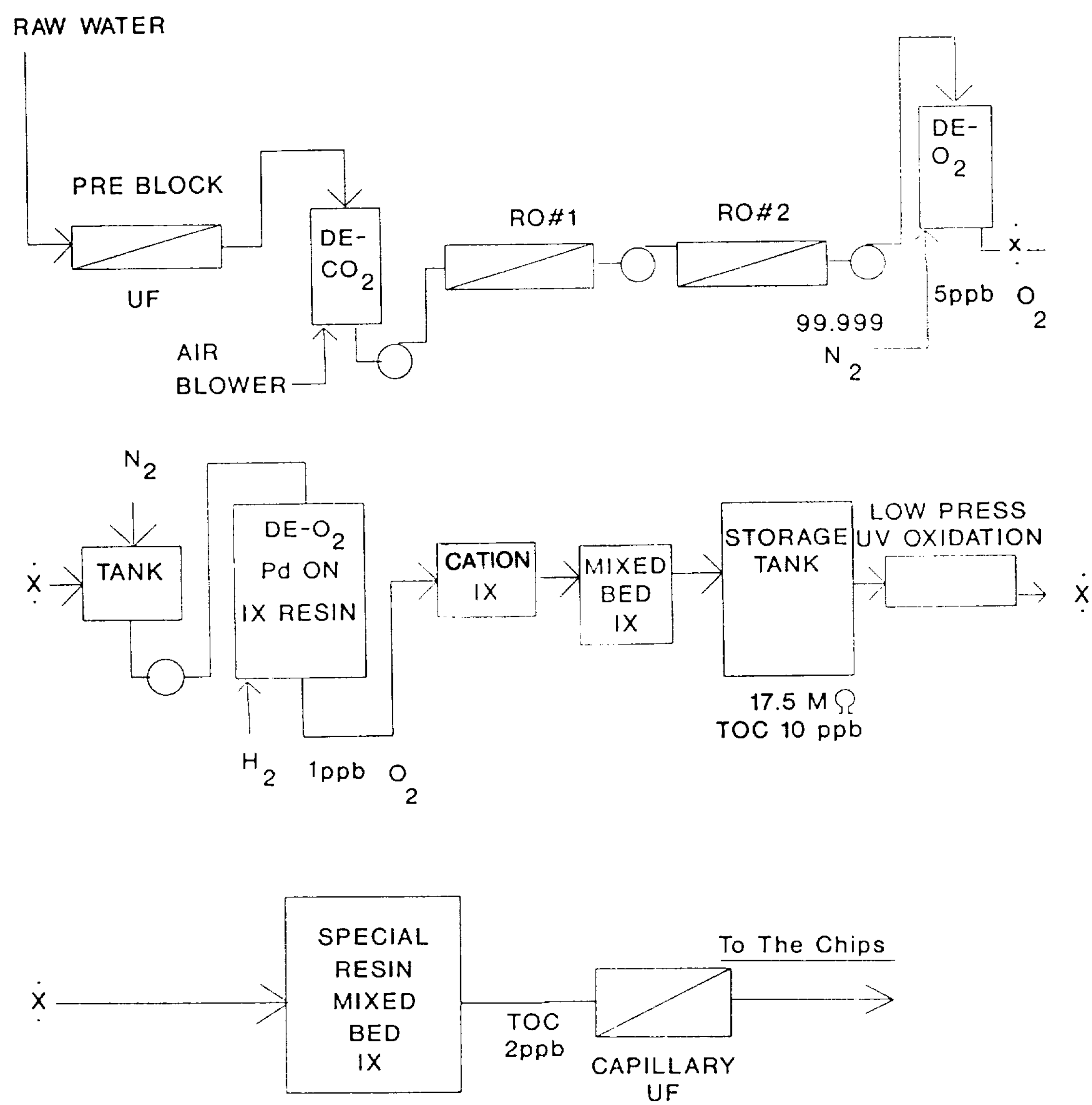


Figure 3.1. Kurita's Water Purification Process

Table 3.1
Specifications for 16 Mb Quality Water

SPECIFICATIONS	KURITA	ASAHI-KASEI	OHYA+	NEXT GENERATION
R, M-ohm-cm, 25°	18.1	18.1	18.1	> 18.2
TOC, ppb	< 2	< 1-5	< 10	0 - 5
Particles/liter 0.05 μm	< 5000	< 5000	< 10,000	1,000
Microorganism counts/liter	< 1	< 1	< 5	< 0.1
SiO_2, ppb	< 1	< 0.1-0.5	---	< 0.5
Dissolved O_2, ppb	< 10	< 5-10	< 50	1
Total metals, ppt Na and higher	< 10-50	< 10-50	---	1

+ H. Ohya, 'State of the Art Ultrapure Water Production in Japan,' *Desalination*, 80 (1991) 159-165.

This sort of difference between the two nations is common. Each has its advantages and drawbacks.

Japanese firms operating in the United States do not often import a Japanese water system. In fact, excellent water systems are available in Europe, the United States, and in Japan (Hango 1992).

The issue of dissolved oxygen is the greatest difference that the panel found between the U.S. practice and that in Japan. In the United States, bacteria are a much greater cause of concern than is O_2. U.S. fabricators seem to have learned to live with O_2. Coupled with the fact that O_3 is an excellent way to kill bacteria and simultaneously reduce organic matter, some U.S. fabricators think that the use of O_3 gives them an excellent cost/benefit ratio.

A major equipment difference is in the form of the final filter. U.S. practice is to use pleated cartridge filters. In Japan, the common practice is to use capillary ultra filters operated with shell side feed. Conceptually, the Japanese approach makes more sense, since the opportunity for picking up particles after the membrane is much greater with the pleated device. But it is hard to argue with the facts, and the use of pleated cartridges gives excellent water. Current final filters have nominal retentions of 0.04 μm, which is approaching the limit of the technology for a pleated microfilter.

Other separations processes needed to produce ultrapure water are well based in both the United States and Japan. For many years the United States has been the leader in ion exchange resins and in membranes generally, but excellent technology is available in both countries. Recent Japanese advances in ion exchange resins permit production of extra high purity resin for the final mixed bed exchanger superior to material produced in the United States. Levels of impurity adsorbed on the resin and its low loading of organic solutes make the material superior to that produced in the United States (Albright 1992).

As shown in Table 3.1, impurity levels are already extremely low. Future requirements for water are not yet firmly established. The role of water in improving chip yields is known only to an extent. Some criteria are of known importance, but most are speculative. For instance, the traditional rule of thumb is that the largest particle should be 0.1 times the characteristic feature dimension. Levels measured in ppb already represent extreme purity (human life expectancy is less than 2.5 billion seconds) and specifications are now quoted in parts per trillion (ppt)! Cost is always an issue. Japanese manufacturers have traditionally been willing to pay more for tighter specification inputs. When those costlier inputs drive variance out of a system, lower cost products may result.

Kurita representatives stated that the major problems facing the next generation water requirements were dissolved organics and metals. TOC tends to leach out of ion exchange resins, membranes, and polymeric piping and seals. Specially passivated stainless steel reduces the TOC problem, but may result in an increase in metals.

Kurita indicated that the cost of water has been linear in the logarithm of chip capacity for many generations. Water cost is rising, but at a predictable, steady rate. Projections for moving beyond 16 Mb are for an increase in water cost significantly above the historic trend. Kurita was optimistic that technology will permit the cost of next generation water to be more in line with the trend. Innovation is required to meet that optimism. It seemed to the panel that the climate for that innovation was better in Japan than in the United States.

REFERENCES

Albright, R. 1992. Rohn and Haas. Private Communication (August).

Balazs, M. K. 1992. Balazs, Balazs Analytical Laboratory, Sunnyvale CA 94086. Private Communication.

Hango, R. 1992. Private Communication.

Leachman, R. 1992. University of California at Berkeley. Private Communication (June).

Ohya, H. 1991. "State of the Art Ultrapure Water Production in Japan." *Desalination* 80:159-165.

CHAPTER 4

SEPARATIONS WITH LIQUIDS

Edward L. Cussler

INTRODUCTION

Separations of liquids in Japan appear to be effected largely along conventional lines. Distillation is common; absorption and extraction are often used; and adsorption is a last resort, used especially for pollution control of dilute solutions. In this sense, the existing Japanese practice is much like that in the United States.

Japanese innovation in this area centers on membranes, especially in the mode of pervaporation. Pervaporation can be an energy efficient alternative to distillation. Current Japanese efforts follow the European focus on ethanol-water separations, with surprisingly little mention of other systems. The JTEC panel was especially surprised to find little mention of pervaporation for pollution control or for aliphatic-aromatic separations.

Other areas of innovation cluster around supercritical extraction and adsorption. Supercritical extraction emphasizes natural product separation, an echo of the original European work on decaffeinating coffee with supercritical carbon dioxide and more recent work with flavors and food products in various locales. Innovative adsorption includes both racemic separations and hollow fibers made of activated carbon.

The panel's trip also reflected two other major trends in Japan that borrow ideas from liquid separations. One is the continuing development of high performance secondary batteries, which will be central to the development of widely useful electric cars. Several groups mentioned using membranes as battery separators and cathodes, but were reticent about details. A second trend is the apparently firm decision to replace chlorine with ozone in water treatment. New technology developed along these lines could spark adoption in the United States.

PERVAPORATION

What is it?

Pervaporation uses a membrane to separate a liquid feed into a membrane-permeable vapor and a membrane-impermeable liquid. The process is shown schematically in Figure 4.1. By convention, the entering liquid is referred to as the feed, the membrane-permeable vapor is called the permeate, and the membrane-impermeable liquid solution is called the retentate. The concentrations of permeate and retentate are determined by the feed concentration, the relative volatility of the species fed, and the relative permeability through the membrane of these species.

Pervaporation can produce major energy saving in chemical separations because it depends on both volatility and permeability. These potential savings are best illustrated by an example, the recovery of 3 percent acetic acid in water. Since acetic acid is less volatile than water, it would be necessary to take all the water overhead in a distillation. The volatilities of acetic acid and water become close at low concentrations of acetic acid in water. Therefore a high reflux ratio would be required, consuming still more energy. For these reasons this separation is commonly accomplished by solvent extraction, which brings its own complications, e.g, the need for regeneration. In contrast, the energy required for the pervaporation can be less than 10 percent of that required for the distillation, a major savings. Moreover, since the heat required is that to evaporate the permeate, pervaporation is especially suited to removal of a lesser constituent.

Current Practice

The panel's survey of pervaporation will be most easily organized around three issues: targets for separations, membranes, and membrane modules. Each merits discussion.

The targets for pervaporation include some of the largest separations practiced in the chemical industry. These include alcohol from water, aliphatic from aromatic hydrocarbons, and trace organics in water. The alcohol-water separations have been a European focus, led initially by research at the University of Nancy. Aliphatic-aromatic separations are being actively pursued by Exxon; publicly available details are largely in patents. The trace organic separations are actively pursued by a small U.S. company, MTR of Palo Alto.

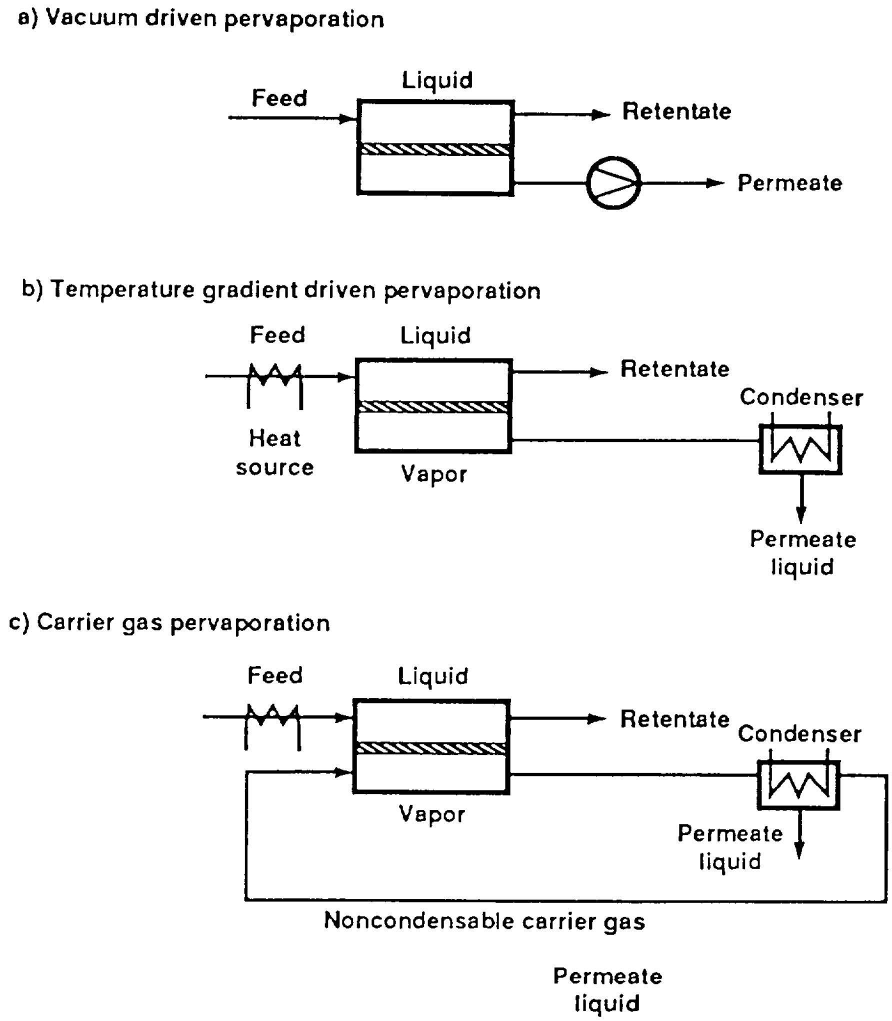


Figure 4.1. Schematic Pervaporation Processes (from R.W. Baker, "Pervaporation," in *Membrane Separation Systems*, DOE report, March, 1990).

Pervaporation membranes can give high selectivities without exotic chemistry. For example, membranes for the alcohol-water separation, commercially available from the German firm GFT, are polyvinyl alcohol. The Exxon membranes are more exotic copolymers, consisting of a monomer giving selectivity, a monomer giving strength, and a crosslinking monomer. The earlier membrane modules, like those of GFT, are of a plate-and-frame design. More recent geometries, including those by MTR, are spiral-wound modules. If parallels with other membrane separations are valid, one would expect an evolution from plate-and-frame to spiral-wound to hollow fibers, and then a return to the geometry that is most economical for a particular case.

Japanese Efforts

Japan's efforts on pervaporation are sound, perhaps somewhat behind the United States, which in turn is behind Europe. Three applications stand out: ethanol-water separations, isopropyl alcohol-water separations, and trace organic separations. The alcohol-water system is being pursued by the Research Institute for Polymers and Textiles (RIPT; part of MITI), by Daicel, by Tokyo University and by Mitsui. RIPT is investigating two types of plasma treated membranes. In the first, a copolymer of acrylic acid and HEMA (a polyacrylic gel) is grafted onto a microporous polypropylene support. The resulting nonporous membrane, which has a 10 μm active layer, is selective for water over ethanol. The second of RIPT's membranes grafts fluorocarbon onto polysulfone, using the plasma treatment to obtain a flexible coating. This membrane, with an active layer of 1 μm, has a selectivity for ethanol over water of about ten and a flux about twice that of GFT. Daicel is reported to be preparing polyacrylonitrile hollow fibers with carboxylic side chains for this system, but the panel learned no details. Professor Kimura at Tokyo University is developing poly (tetramethylsilylpropylene) membranes for the same purpose. A group in the Industrial Products Research Laboratory, a MITI effort at Tsukuba led by Dr. Sumio Yamada, has similar goals. Mitsui is handling engineering in Japan for the industry's leader, GFT. In all these efforts, the thrust seems to be to improve on the accomplishments of the Europeans, and not to invent.

Pervaporation of isopropyl alcohol-water systems has been well developed by Tokuyama Soda. This company sells a hollow-fiber based process for concentrating aqueous isopropanol from about 88 percent to 97 percent. While the composition of the current membrane was not revealed, a future membrane might be based on chitosan, whose selectivity of 2,400 should easily allow producing 99 percent isopropanol. Tokuyama Soda's sales are largely to the electronics industry, which uses these units to recycle solvents in clean rooms. This seems to be an attractive market, serving an industry where Japan is a world leader.

Pervaporation of trace organics, often called volatile organic compounds (VOCs) by civil engineers, was often mentioned as promising, but few seem to be working on this. Kyushu University and the Nippon Oil and Fats Company apparently have a collaboration with the Russian group of Dr. Plate, but few details are available. RIPT mentioned separating trichloroethylene, but this once-standard dry cleaning solvent will soon be replaced by legislative fiat.

An innovative pervaporation project, suggested by Dr. Kensaku Mizoguchi of RIPT, is the use of pervaporation as a means of removing trace amounts of organics from groundwater. Membrane modules are buried in the ground near the pollutant flume. Water containing pollutant is free to percolate into the shells of the modules. Air is pumped underground and blown through the fibers, and the organics permeate the air stream. An activated-carbon adsorption bed can then be used to remove the organics from the air before it is released to the atmosphere.

Other related membrane work is more scattered. Membrane distillation, a focus for Dr. M. Tanigaki at Kyoto University, is similar to pervaporation but uses a porous, nonselective membrane, often to make cold fresh water from hot seawater. This work seems consistent with efforts in Europe and Australia. Work in Professor S. Kimura's group at Tokyo University relates membrane fluxes with fugacity based driving forces, and studies in the Industrial Products Research laboratory at Tsukuba measure membrane sorption. These seem similar to efforts elsewhere in the world.

A Note on Distillation

The panel also heard mention of a method for making distillation more efficient by heat integration. This method, which involves running part of the distillation column under a different pressure than the rest, has been theoretically developed by, among others, Professor Richard Mah of Northwestern University. U.S. industry has rejected these ideas as requiring too large of a capital investment. The panel could not tell how the Japanese hope to circumvent these apparent economic constraints.

ABSORPTION AND EXTRACTION

What are they?

Absorption and extraction are major separation processes in the chemical industry, exceeded in importance only by distillation. They are very well established. They are a fixture in every chemical plant and in every chemical engineering curriculum, and have been for over fifty years.

The basic process for these operations is best illustrated by an example of carbon dioxide absorption. The equipment for this process, called a "packed tower," is essentially a piece of pipe mounted vertically and filled with inert packing, sometimes shaped like ceramic potato chips. Gas containing carbon dioxide is blown upwards through the tower, as suggested in Figure 4.2. Water, often containing reactive amines, trickles downwards through the tower, absorbing the CO_2 as it falls. Because this liquid is spread out on the packing, it has a large surface area per volume of tower. This large surface area per volume insures rapid adsorption and hence efficient tower operation. This large area per volume is a general goal of all absorption and extraction. The terminology and the equipment used can look different for extraction (Fig. 4.3), but the basic ideas are the same.

Current Practice

These traditional areas currently show little change, a reflection of their maturity. The current practice is most easily organized around the targets for separation, the liquids used for these separations, and the geometry of the equipment. Each merits review.

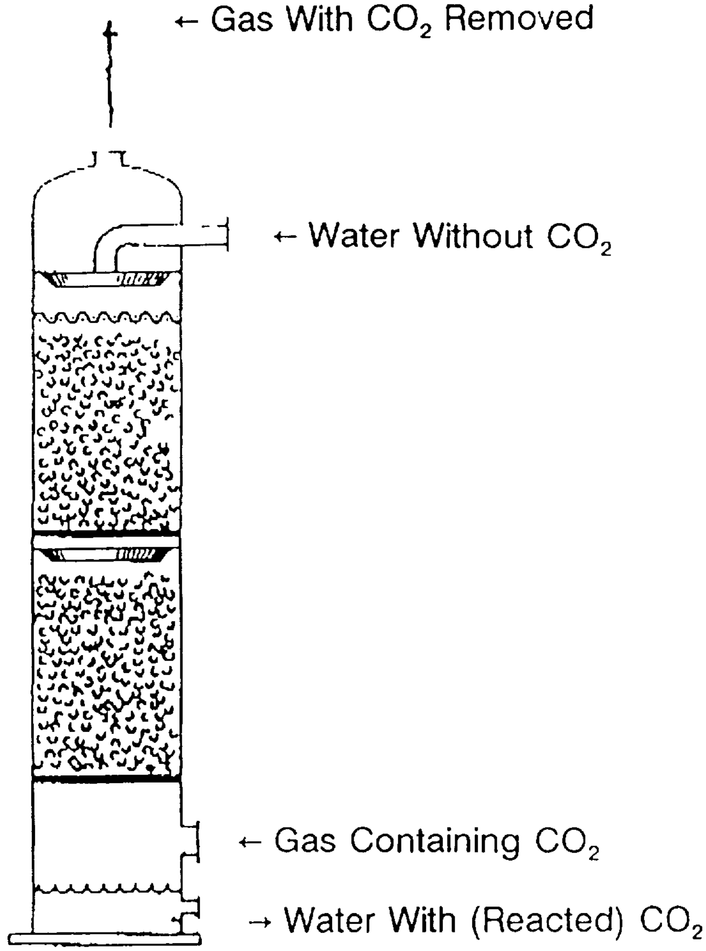


Figure 4.2. A Packed Tower for Gas Absorption. The packing is an inert ceramic.

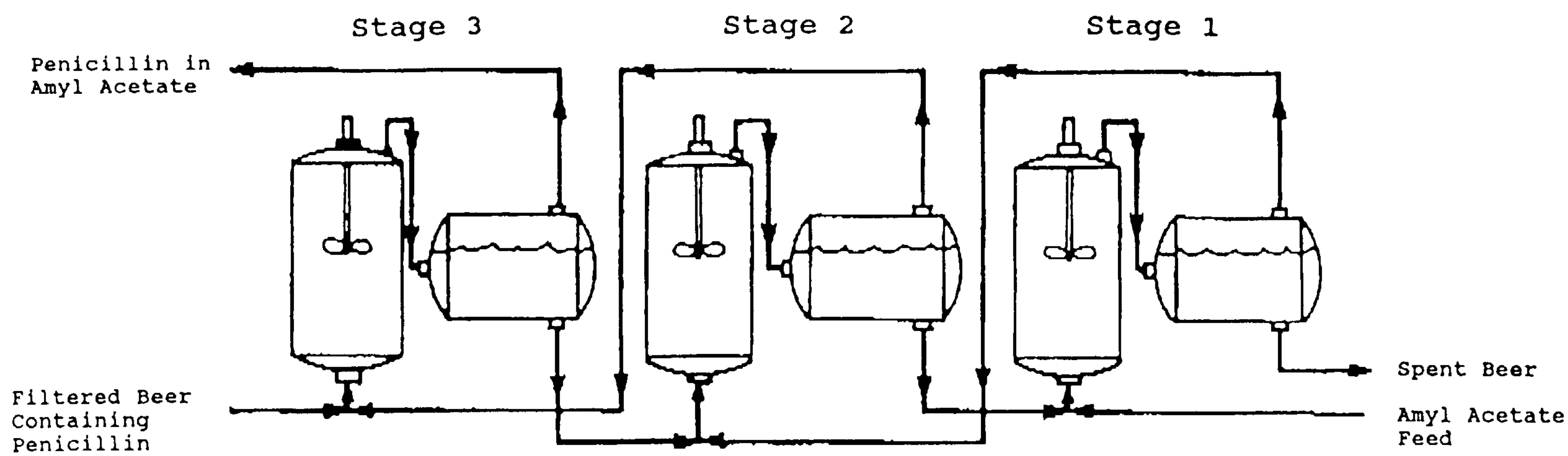


Figure 4.3. An Example of Liquid Extraction. This case is for penicillin (Belter et al., *Bioseparations*, Wiley, 1986).

The targets for gas absorption center on the so-called acid gases -- carbon dioxide; hydrogen sulfide and the sulfur oxides; and the nitrogen oxides. Other major targets include ammonia and oxygen. This last is rarely considered in the chemical industry, but is basic to sewage treatment, and hence is of major concern for many civil engineers. The solutes separated by extraction vary much more widely. The largest extraction process is the dewaxing of lubricating oils (or "lubes"), required so that wax crystals do not form in the crankcases of cold engines. Other solutes purified by extraction tend to have high value, e.g., dyes, flavors, and many drugs. The liquids used for gas absorption center on alkyl amines, which react with acid gases at low temperature. These reactions are usually easily reversed at higher temperature to remove, or "strip," the absorbed gas. In the United States, amines whose reactions can be reversed by changes in pressure, not in temperature, have allowed cheaper, energy-saving separations. The liquids used for extraction, like the solutes to be separated, vary widely. Some engineers claim that every known solvent has been tried for the dewaxing of lubes. Trends include seeking less carcinogenic solvents, especially substitutes for methylene chloride. These do not seem especially hard to find. This concern with less carcinogenic solvents has focused attention on extractions with liquid or supercritical carbon dioxide, a focus of research in Japan that is described later in this chapter.

The third topic for absorption and extraction is the equipment geometry. Current work in the United States centers on high efficiency packing, an expensive but effective alternative to the simple ceramics mentioned above. Other less developed efforts of innovation include using membranes to provide the large surface area per equipment volume that is the grail of these separations. Japanese work on these three topics -- solutes to be separated, the solvents used, and the equipment geometry -- is reviewed in the following three sections.

Japanese Efforts on Absorption

Japan's efforts on gas absorption are largely scholarly extensions of existing knowledge. Their overall effort is similar to that in the United States, and perhaps somewhat behind that in Europe. Major breakthroughs anywhere in the world seem unlikely.

There are also Japanese efforts to remove carbon dioxide from stack gas and convert it into alcohols. Efforts on this topic, which are also discussed in the chapter on gas separations, include studies with amines and with CO_2-selective membranes, both at the University of Tokyo and at the Research Institute of Innovative Technology for the Earth (RITE) at Kansai Science City. Both projects are MITI supported. These efforts could be aided by the fundamental studies of Dr. T. Nitta at Osaka University.

The panel was impressed with Toray's efforts to use spiral-wound membrane contactors as a new geometry for gas absorption. Toray sees four major markets for these membrane contactors -- boiler feeds, hemodialysis, ultrapure water, and soft drinks. All are commercial, although the last two are better developed. Toray's system for membrane contactors uses a silicone membrane in a spiral-wound module. Some modules collect the gas removed by drawing a vacuum on the central tube. Other, more efficient modules might plug the central tube, and separate the membrane envelope with a glue line, running from the tube to near the end of the module. A sweep stream of nitrogen enters the end of the tube, spirals outward to the end of the glue line, rounds this glue line, and spirals back to the central tube (Fig. 4.4). Modules with a sweep are typically twice as effective as modules run with vacuum alone.

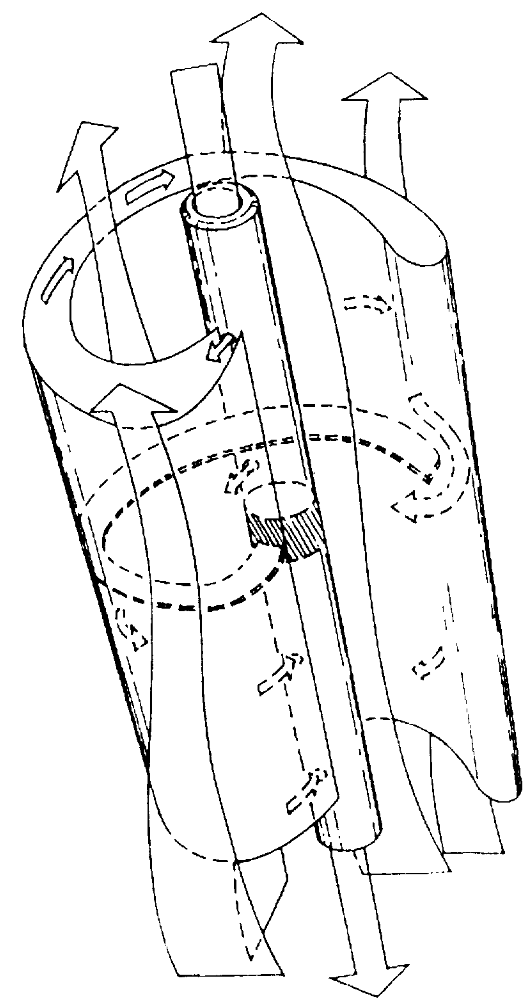


Figure 4.4. The Expected Design for the Toray Membrane Contactor. The sweep gas enters and leaves in the central tube.

The performances of the modules, characterized with an overall mass transfer coefficient times a total membrane area, cannot be completely analyzed from the fragmentary data given. These data suggest an area per volume around 30 cm^2/cm^3. On the other hand, Toray's own analysis results in a figure of 8 cm^2/cm^3. The data Toray supplied to the panel also appear to imply that about half the resistance to mass transfer comes from the nonporous silicone membrane. Neither of these values is especially good.

Still, Toray has made these systems work commercially. Their performance is perhaps one-fourth of that routinely produced by U.S.-made contactors. However, Toray has delivered working systems. As a result, Toray's accomplishments command respect.

Japanese Efforts on Extraction

Logically this section should analyze separation targets, appropriate solvents, and innovative equipment. But since separation of metals is treated in Chapter 5 with all metallurgical extractions, a significant thrust in supercritical extraction is analyzed below.

Japanese work on supercritical extraction has two interesting features -- the choice of systems and the development of equipment. The choice of systems emphasizes extraction of natural products. For example, N. Ikawa at Kobe Steel has separated polyunsaturated fatty acids from vegetable and fish oils by continuous supercritical extraction. This process is under development for commercial use. The same group is studying batch analogues for supercritical extractions of flavors and colors from plants, of pharmaceutical chemicals, and of ethanol from water. This last topic, an effort to avoid azeotropic distillation, is in the pilot-plant stage. Dr. Sako at the National Chemical Laboratory for Industry in Tsukuba is trying to produce furfural from hemicellulose under supercritical conditions. In this analogue to reactive distillation, the supercritical carbon dioxide dramatically represses side reactions that severely compromise the nonsupercritical reactor.

The panel was impressed with Kobe Steel's efforts to cut the high cost of supercritical extraction, a high cost that frequently inhibits use of this technology. Kobe Steel has traded on its experience in high-pressure technology and fabrication to produce skid-mounted plants suitable for supercritical fluid extraction. The object seems to be to produce high-quality units for sale at reasonable cost. There do not appear to be innovations in the supercritical fluids used or in the type of equipment. However, a number of existing commercial uses were cited, several of which appear to serve specific Japanese needs (e.g., extraction of herbs, fish and vegetable oils).

Japanese Efforts on Liquid Membranes

The last topic is a special one, where the Japanese have continued to be active long after their peers in the United States and in Europe have moved to other areas. This is the development of liquid membranes, also known as solid-supported liquid membranes. These are commonly thin films of liquid solution stabilized within the pores of a microporous polymer support. Such composite liquid membranes are more commonly used for extraction than absorption, so the extraction case is that described here. In most applications, the liquid membrane is an organic solution that separates an aqueous feed and an aqueous stripping solution. The feed typically contains a mixture of solutes, one of which is selectively extracted into the liquid membrane. This solute diffuses across the membrane and into the adjacent stripping solution, often because that stripping solution has a different pH than the feed. Thus liquid membranes equate conceptually to two extractions. Because these two extractions are compressed into a 30 μm liquid layer, they can be dramatic; a brightly-colored solute can be moved from low concentration to high concentration across the membrane, via the magic of the uncolored pH difference.

Liquid membranes are not stable over long times, and so have not been widely commercialized, in spite of major investments in this area by large multinational corporations. In spite of this, Japanese efforts continue. Fully one-third of Japanese contributions to the International Solvent Extraction Congresses have been on this topic. On this trip, the JTEC panel saw two scientifically sound examples. K. Hiratani at the Industrial Products Research Laboratory is trying to make inexpensive polyethers that can selectively complex specific ions, paralleling an earlier U.S. effort by 3M. Dr. Hiratani can perform isotope separations similar to those realized at the Wright Patterson Air Force Base. Dr. T. Shino at the National Chemical Laboratory for Industry, Tsukuba, has made liquid membranes based on Donald Cram's Nobel Prize winning chiral crown ethers. These give separation factors of twenty, an excellent value, but at low fluxes, on order of 10^{-10} mole/cm^2-sec. Significantly, this chemistry is used by Daicel for commercial adsorbents, but not for liquid membranes.

The panel does not understand the Japanese fascination with liquid membranes, or see what advantage they hope to gain with these developments.

ADSORPTION FROM LIQUIDS

What is it?

Adsorption involves capturing dissolved solutes on a microporous solid substrate as shown in Figure 4.5. The result is a liquid effluent without solutes, and a solid saturated, or "loaded," with solutes. Sometimes the loaded solute is stripped and recovered; sometimes the loaded solid is discarded. While adsorption can be used to treat both gaseous and liquid solutions, an analysis of only liquid solutions follows. By focusing on liquids, the discussion is restricted to the types of adsorption that are also called "frontal chromatography" or "liquid chromatography."

Current Practice

Effective adsorption requires an adsorbent that has a large surface area on an inert matrix. Adsorbent surface areas routinely exceed 100 m^2/g, and can be as high as 2,000 m^2/g. Common examples include silica, alumina, activated carbons, zeolites and ion exchange resins. The carbons are sometimes made from vegetable material like coconut shells, and may retain traces of the original biological skeletons. The ion exchange resins are frequently used as hydrophobic adsorbents, as well as for their ionic capacities.

Adsorption is one of the most effective separation processes for dilute solution, and hence is often mentioned for pollution control. It is expensive. After all, in separating solutes from dilute solutions, adsorption is using a lot of free energy. Regenerating the adsorbent will take even more free energy.

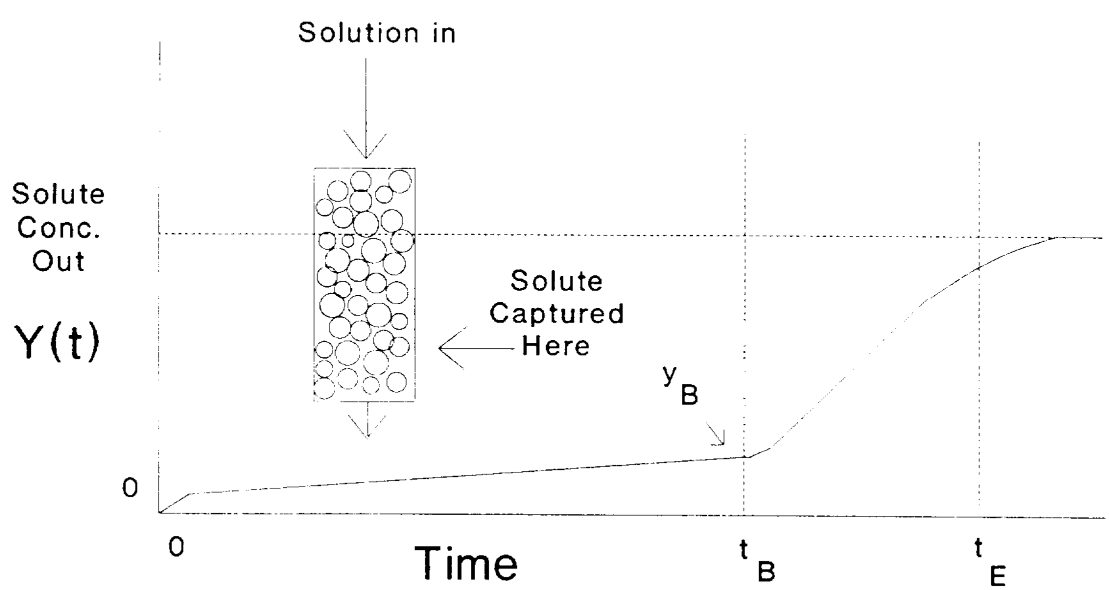


Figure 4.5. A Typical Adsorption. The solute concentration entering the column is high; that leaving the column is low until some breakthrough time t_B.

Japanese Efforts

The efforts are most easily organized around chromatographic systems, adsorbent chemistry, and chiral separations. The leader for chromatographic systems is apparently Kurita. Hirotashi Motomura, Manager of Kurita's Chromatography Division, asserts that his division has 70 percent of the Japanese market for preparative high pressure liquid chromatography (HPLC) columns.

These systems are either developed in-house or sold under license. The columns are currently up to 60 cm in diameter, and use pressure drops to 70 bars. The packing or stationary phase is 50--150 μm spheres, most commonly of silica gel. Ion exchangers are rarely used. The panel's impression is not of innovation, but of reliable implementation.

Adsorbent chemistry seems largely primitive, as it is in the United States. Several individual systems, many developed in universities, are interesting. Professors Okagaki and Tamon of Kyoto University have developed metal impregnated carbons as carbon monoxide adsorbents. Loading is said to be unusually high, over 20 percent by weight. Professor Shigeo Katoh, also of Kyoto University, uses short polypeptides as a stationary phase for affinity chromatography. Professor Suzuki of the University of Tokyo uses pyrolyzed fibers of activated carbon as an alternative adsorbent geometry, a method explored by Monsanto and others. Toray's "Ionex" ion exchange fibers are said to be effective for immobilizing proteins, possibly for biocatalysis. These efforts parallel the diversity and the quality of those in the United States.

In the area of chiral separations, Japan seems even with the United States, and may pull ahead on industrial-scale separations. Chiral mixtures are of species with identical chemistry but different geometry; they are mixtures of "right-handed" and "left-handed" molecules. Such separations are extremely difficult. At present, they are largely accomplished by chromatography, using a variety of stationary phases. Those synthesized by William Pirkle of the University of Illinois are especially effective and especially expensive. Since chromatography is often less effective on a large scale, racemic extraction is also occasionally used. Large-scale crystallization can be effective, though it cannot often be applied. One recently successful public offering by the U.S. company Sepracore depended on racemic separations with largely unproven membrane reactors.

Japan's efforts on racemic separations appear to center on chromatography. Daicel offers a wide variety of stationary phases for this type of separation, comparable to those sold by Pharmacia and others. Daicel's offerings include the same chiral crown-ether compounds based on Donald Cram's Nobel Prize-winning work, synthesized by the National Chemical Laboratory for Industry, and ineffectively used in liquid membranes. Academic research in this area seems scattered. For example, Dr. Masawaki, an associate of Professor I. Komasawa at Osaka University, has tried to extend similar ideas to membranes.

Daicel has made a major step to extend this technology. Daicel employees M. Negawa and F. Shoji, have recently reported racemic separations in a "simulated moving bed" (Negawa and Shoji 1992). A simulated moving bed is a technology developed in the United States by UOP and used effectively for large-scale separations of liquids. By adapting it to racemic mixtures, Daicel has increased productivity by about sixty times over conventional adsorption technology.

Whether this is important depends on the U.S. Food and Drug Administration (FDA). The FDA recognizes that many drugs are racemic mixtures, and that pure isomers can be more effective and less toxic. Recently, the FDA has suggested that pure isomers may be treated as new drugs, circumventing existing patents. Pure isomers might be made by biochemical or microbial synthesis, but this method is typically five times less efficient than racemic synthesis. Thus there appears to be a significant incentive to separate racemic drugs, a separation where Daicel's simulated moving bed may be a technical breakthrough.

REFERENCES

Baker, R. W. et al. 1990. *Membrane Separation Systems - A Research & Development Needs Assessment*. Report No. DOE/ER/30133-H1. U.S. Department of Energy.

Belter et al. 1986. *Bioseparations*. John Wiley & Sons.

Negawa, M. and F. Shoji. 1992. *Journal of Chromatography* 590: 113-7.

CHAPTER 5

HYDROMETALLURGICAL SEPARATIONS

Milton E. Wadsworth

INTRODUCTION

Smelting Practice

While the main focus of this evaluation is on aqueous solution (hydrometallurgical) metals separation, the Japanese smelting industry must be considered because important aqueous processing steps (mainly leaching, purification, electrorefining and electrowinning) are included in smelting practice. The processing of zinc concentrates in Japan is predominantly by the roast-leach-electrowin (RLE) process, of which hydrometallurgy is a major component. Commercial application of hydrometallurgy is strongly coupled with the smelting industry.

The Japanese smelting industry is among the most modern in the world (Everest Consulting Assoc. 1982). Newly applied technology has focused mainly on problems related to the environment and on the production of value added materials. The copper smelting industry of Japan grew dramatically in the 1960s and has remained one of the largest in the world since 1970 (U.S. Congress, Office of Technology Assessment 1988). During the period 1955 to 1975, the Japanese copper smelting industry increased tenfold, providing opportunity to introduce new technology (Ishikawa 1985). The first Outokumpu flash furnace outside of Finland was constructed in Japan. A basic strategy was to take advantage of value added resulting from raw materials processing. During the period of rapid growth, the need for close environmental control became a major concern. Also, new construction provided the opportunity to improve environmental integrity. Noteworthy advances have been made in waste gas handling systems, control of fugitive gases, handling of smelter dust, and treatment of waste water high in arsenic and heavy metals (U.S. Congress, Office of Technology Assessment 1988). After 1980, Japan entered into a series of projects to assure continued import of copper concentrates. Ventures in Columbia and Chile and equity positions with Chino Mines in New Mexico and Morenci in Arizona helped assure sources of copper concentrates. Japan is the world's largest importer of copper concentrates. In 1986, Japan imported over 837,400 metric tons of concentrate, amounting to 60 percent of concentrate destined for market economy countries (U.S. Congress, Office of Technology Assessment 1988). Japanese statistics on nonferrous metals production for 1989 are presented in Tables 5.1 and 5.2.

Table 5.1
Production of Nonferrous Metals in Japan, 1989
(1000 metric tons)

Commodity*	Copper	Zinc	Lead	Nickel
Domestic C	6.4	135.9	36.4	
Imported C	894.9	471.8	170.2	
Other C	97.4	77.4	53.0	
Total	998.7	685.1	259.6	22.1
Imported M	524.0	126.8	62.5	44.5
Total Supply	1,522.7	811.9	322.1	66.6

* C = Concentrates; M = Refined Metal (Source: Kogyo Binran, *Statistics 1989*)

Table 5.1 presents the figures for nonferrous metal production in Japan. Table 5.2 presents world production figures for nonferrous metals. Japan imports the majority of its aluminum because of the high cost of electrical energy. There is one aluminum plant in Japan that imports bauxite and produces cell-grade alumina by the Bayer process.

In the United States, copper smelters are located near mine sites. In Japan, smelters are on or near the coast, facilitating delivery of concentrates and shipping of copper and sulfuric acid. The United States has an estimated 19 percent of the world's minable reserves and is about 85 percent self-sufficient (Everest Consulting Assocs. 1982). Japan's production of copper from domestic mines is small (Table 5.1), but it ranks fourth among major copper smelting countries (Table 5.2).

Table 5.2
World Nonferrous Metals Production, 1989
(1,000 metric tons)

	Copper		Zinc		Lead	
RANK	**NATION**	**AMOUNT**	**NATION**	**AMOUNT**	**NATION**	**AMOUNT**
First	U.S.	1,953.5	Soviet Union	1,020.0	U.S.	1,169.0
Second	Soviet Union	1,355.0	Canada	669.7	Soviet Union	750.0
Third	Chili	1,071.0	Japan	663.8	England	350.0
Fourth	Japan	989.6	China	450.9	Germany*	349.8
Fifth	Canada	511.2	U.S.	358.2	Japan	332.4
Sixth	China	470.1	Germany*	353.5	France	301.9
	Others	4,527.1	Others	3,708.2	Others	2,572.6
TOTALS		**10,877.5**		**7,244.3**		**5,825.7**

* West Germany

(Source: Kogyo Binran, *Statistics of 1989*)

The Japanese smelting industry has benefitted by being able to introduce advanced world technology into its plants. The United States has had to deal with old plants and the necessary economic cost of upgrading these plants during the economic downturn of the early 1980s. The recent upturn of the copper market has permitted major upgrading of the copper industry in the United States. New plant construction, automation, and advanced materials handling technology is resulting in renewed U.S. capability to compete worldwide.

Japan is the world's third largest producer of refined zinc. In the United States, there has been a major decline in zinc production during the past forty years. Between 1955 and 1982 the number of operating zinc smelters decreased from 18 to 5 (Everest Consulting Assocs. 1982), and today the United States is only approximately 30 percent self-sufficient in zinc production (Mineral Industry Surveys 1988). Japan has made major strides in applying worldwide technology to the smelting industry and has made significant advances in the area of environmental control, energy efficiency and cost reduction.

Hydrometallurgy

In scope, hydrometallurgy involves the leaching of ores and concentrates, solution upgrading, and purification and recovery of metals by precipitation or by chemical or electrochemical reduction. Solvent extraction and ion exchange are important technologies for the upgrading of aqueous solutions prior to electrowinning and precipitation. In the U.S. copper industry the leaching of very low grade ores (dump leaching) represents an important application of hydrometallurgy, as are heap and vat leaching. In 1978, in the western United States, the production of copper by leaching was approximately 18 percent of the total copper production. While this has varied during the last few years because of major changes in the copper industry, it is expected that leachable material from mining will continue to range from 15 percent to 20 percent.

Rapid growth in gold recovery by cyanidation has occurred in the United States in recent years. The application of heap leaching is increasing rapidly and is remarkable for its economic application to very low grade ores (e.g., less than 0.07 oz/ton) and, in one example of dump leaching, to material less than 0.03 oz/ton. The leaching of low grade ores generally is not a technology employed in Japan. Japan receives concentrates of base metal sulfides and higher grade run-of-mine ores, and therefore has little involvement in the application of hydrometallurgy to the leaching of these materials.

In general, hydrometallurgy has not succeeded in displacing smelting as a method for treating base metal sulfide concentrates, although it remains an important component of conventional smelting technology. Noteworthy exceptions are the Sherritt Gordon nickel leaching plant in Fort Saskatchewan, Alberta, Canada, and the recent (1981) pressure zinc sulfide leaching process developed by Cominco, Ltd., at Trail, British Columbia. Hydrometallurgy generally has higher energy requirements than smelting (U.S. Congress, Office of Technology Assessment 1988) and often requires more stages of treatment. The development of advanced smelting technology has been successful in reducing emissions to the point that they meet environmental specifications both in Japan and in the United States. This, plus energy efficiency and the production of an environmentally acceptable slag, makes smelting the most viable method for the treatment of base metal sulfide concentrates. Undesirable products of smelting are various intermediate products (dusts, fumes, etc.) containing toxic elements such as arsenic, lead and mercury. Hydrometallurgy may play an important role in the future for the treatment of these materials. In smelting, iron is recovered in the slag and rejected with the slag. The slag is quite resistant to weathering and is environmentally more acceptable than are the products of most hydrometallurgical treatment plants. Hydrometallurgical treatment plants normally reject iron in the form of oxides or basic iron sulfates (jarosites) that present environmental problems for the future. Sulfur is rejected as a sulfate or jarosite. Improved technology in iron precipitation has improved zinc recovery but has not addressed successfully some of the major long-range problems associated with the discharge of these materials.

In Japan, major commercial applications of hydrometallurgy are those related to smelting, with RLE treatment of zinc concentrates a prime example. Other applications in Japan are the leaching of specialty materials of high value, recovery of rare and precious metals, and a broad array of research in the areas of leaching, solvent extraction, ion exchange, solution purification, precipitation, electrorefining, electrowinning and processes to improve value-added opportunities, environmental control and recycling.

HYDRO-SEPARATIONS IN SMELTING PRACTICE

Table 5.3 lists the major nonferrous smelters in Japan that employ hydro-separation technology. Included are the names of companies having major ownership and the types of hydro-separation processes that take place. Also included is one uranium hydrometallurgy pilot plant. Figure 5.1 illustrates the location of these plants. Numbers correspond to the numbers in Table 5.3.

Innovation has centered mainly on improving energy efficiency, reducing costs, recycling materials and addressing environmental problems. The Iijima zinc refinery (Onazaki, Sato and Kuramochi 1986) adopted the hematite process (Rupanack 1986) in 1972 because its final iron product is hematite of sufficient purity to be used commercially. This process is more costly than the jarosite and goethite processes, but is environmentally more acceptable. The jarosite and goethite processes dump the iron as basic iron sulfates or hydroxides containing toxic elements such as arsenic, lead and mercury. The hematite process not only recovers iron in marketable form, but also provides a means to remove undesirable toxic contaminants.

OTHER APPLICATIONS OF HYDROMETALLURGY

Metal separation processes in Japan must consider the entire system in such a way that all effluents can be managed in an environmentally acceptable manner. Consequently special emphasis must be given to recycle streams, to separate toxic materials, to prepare pure recycle water with contaminants (including colloidal suspensions removal) reduced, and to develop value-added byproducts and non-reactive solid wastes. Also, special emphasis is given to the recovery of less common metals such as gallium and indium, present in various ores and smelter streams that have value-added potential.

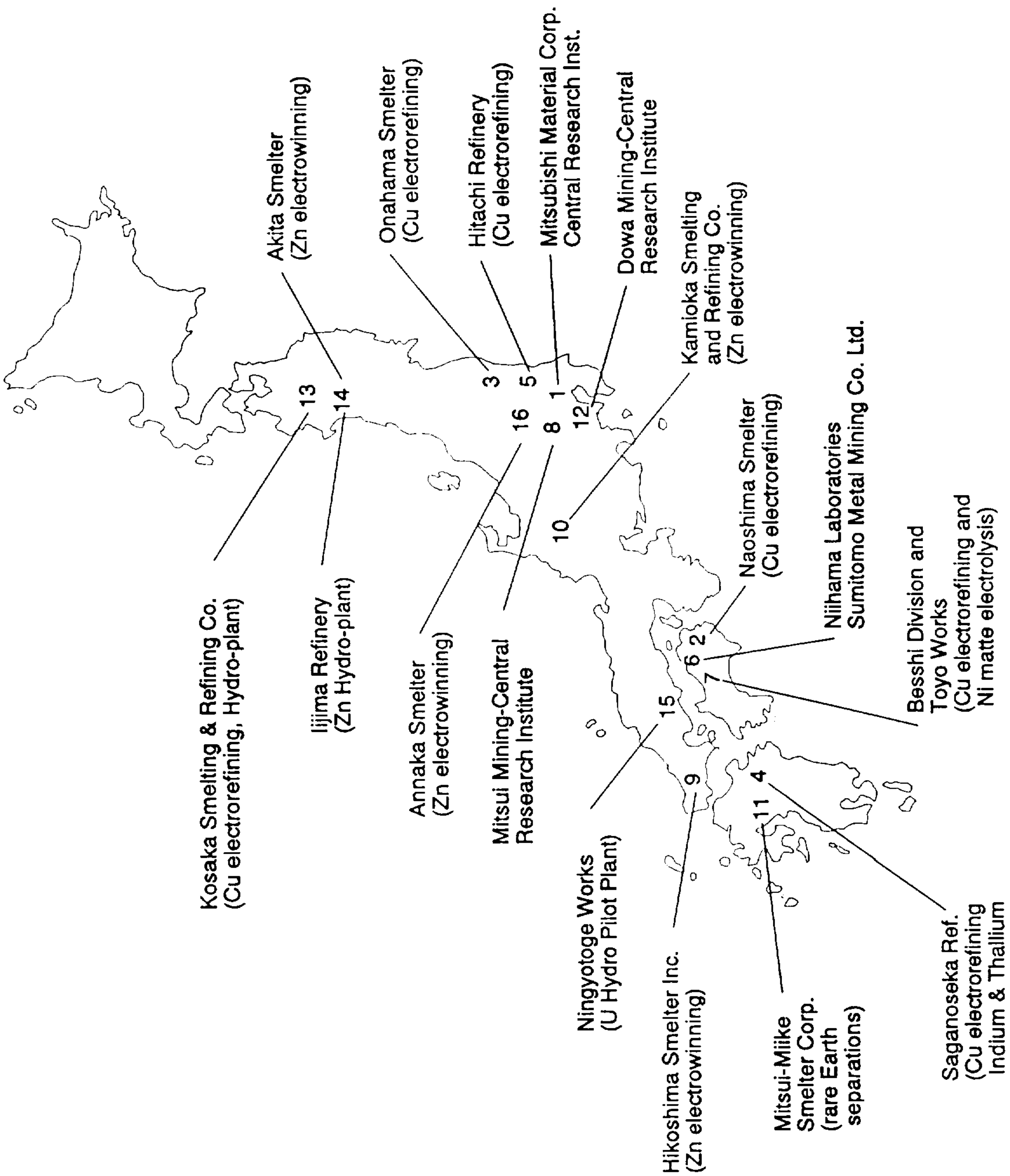


Figure 5.1. Location of Plants with Hydrometallurgical Separations. Included are Plant Research Centers.

Table 5.3
Plants Employing Hydro-Separation of Metals

Company	Plant	Separation Process
Mitsubishi Materials Corporation	(1) Central Research Institute	
	(2) Naoshima Smelter	Copper Electrorefining
	(3) Onahama Smelter	Copper Electrorefining
Nippon Mining Co., Ltd.	(4) Saganoseka Refinery	Copper Electrorefining Indium-Electrowinning Thallium-Electrowinning
	(5) Hitachi Refinery	Copper Electrorefining
Sumitomo Metal Mining Co., Ltd.	(6) Niihama Laboratories	
	(7) Besshi Division and Toyo Works	Copper Electrorefining Nickel Matte Electrolysis
Mitsui Mining and Smelting Co., Ltd.	(8) Central Research Institute	
	(9) Hikoshima Smelting Inc.	Zinc Electrowinning
	(10) Kamioka Mining and Smelting, Inc.	Zinc Electrowinning
	(11) Mitsui-Miike Smelting Inc.	Separation of Rare Earths
Dowa Mining Co., Ltd.	(12) Central Research Institute	
	(13) Kosaka Smelting and Refining Co.	Copper Electrorefining Hydromet. Plant
	(14) Iijima Refinery; Akita Smelter	Hydromet. Plant for Zinc
Power Reactor and Nuclear Fuel Development Corp.	(15) Ningyotoge Works	Hydrometallurgical Pilot Plant for Uranium
Toho Zinc Co., Ltd.	(16) Annaka Smelter	Zinc Electrowinning

Specific examples of commercial, or near commercial, development are:

1. Thiourea leaching of gold-containing silicon ores has been carried to the pilot plant stage by Hishikari Mines in the Kyushu District.

2. A process for the treatment of residues from electrostatic precipitators in electric power generation has been commercialized.

3. A new plant for rare-earth recovery and purification was brought on-stream last year by Hanaoki Rare Earth Co.

4. Tests have been carried out for the treatment of flue dusts produced by iron blast furnaces.

5. Research is continuing for the treatment of dust (high arsenic, etc.) from copper flash smelting operations.

6. Work in the area of comminution has focused on ultrafine grinding. Several new grinding machines are commercially available. These are manufactured by Hosokawa Mikuron Co., Ltd. and Otsuka Tekkon Co., Ltd.

7. In the area of metals recycling, processes have been developed for the treatment of spent catalysts for recovery and purification of metal components, for the treatment of electronic scrap for recovery of gold and other metals, and for the management of Cd in Ni-Cd batteries. Regarding the latter, a new recycling network is currently under proposal by Cd producers.

8. Bioextraction technology is currently employed by the Kosaka Works of Kosaka Smelting Co., Ltd. in the treatment of residues for the oxidation of Fe(II) to Fe(III).

9. Sumitomo Metals and Mining Company has developed a new technology related to the treatment of nickel matte anodes. These are matte anodes of composition Ni_3S_2 from International Nickel Company (INCO). The technology involves the treatment of cuprous chloride for the recovery of HCl used in the process. This research is an extension of ongoing chlorine research that has been used recently for successful treatment of ferrous sulfide concentrates containing nickel. The chlorine reaction produces ferrous chloride plus elemental sulfur and ferrous chloride.

10. In another area, Asahi Chemical Industries Company has been carrying out research for many years on stable isotope separation of U_{238} and U_{235}. This is done by rapid solvent extraction exchange in which approximately 5 million

steps occur with a time constant of approximately 0.1 seconds per stage. Over the last 20 years, approximately ¥30 billion has been expended in this research.

11. In the area of RLE, Japan has achieved a very high state of specialization in its technology. The most recent advances are in energy conservation, and have been achieved in two ways: The plant is automated to work on very high current density during off peak hours and low current density during high peak hours. The low current density must not fall below 50 amps per m^2, or else zinc metal will be redissolved in the system. During the high current density operation the mean current density is 600 amps per m^2, with an average current density of 450 amps per m^2. This has now been adopted generally as part of the roast-leach-electrowin technology.

12. A second method for conserving energy has been a major change in anode spacing from approximately 3 cm to 2 cm. This work has been spearheaded by Mitsubishi Metals Company. The problems that normally would accompany shortening the distance include warpage and the formation of dendrites. These problems are managed by an automated system in which the anodes are loaded into cassettes and handled by an automated mechanical system.

13. Kawasaki Steel Corp. has developed a solvent extraction process for removal of iron from pickling liquor. The process is used at the Chiba Works.

14. Sumitomo Chemical Co. has developed a process for recovery of In from Zn leach residues and recovery of Ga from Bayer solutions by solvent extraction.

15. Sumitomo Metal Mining Co. has developed a continuous silver electrorefining process.

HYDROMETALLURGY RESEARCH

University research in hydrometallurgy covers a broad spectrum of activities from highly theoretical to resource recovery technology. Research at the various institutes and government laboratories is aimed at more specific targets according to the mission of each laboratory. Table 5.4 presents a sampling based on the JTEC team's site visits and on recent literature.

CONCLUSIONS

Japan has made major advances in its smelting and associated hydrometallurgical separations technology to reduce energy consumption, costs and environmental impact (Ishikawa 1985). While the majority of its processes are based on conventional technology, a high degree of improvement has been achieved. In some instances (e.g., the hematite process at Iijima) a more expensive process has been adopted to solve pressing environmental problems.

University research seems to be of high quality but is mainly theoretical. University equipment is generally good, but physical plant conditions are poor and often overcrowded.

There is little research in mineral processing and in the leaching of raw materials. This stems from the fact that most metals are imported in the form of concentrates.

There has been a significant amount of research on the fundamentals of leaching, solvent extraction, ion exchange and chemical and electroreduction. There does not seem to be a strong linkage between universities and industry for technology transfer. Examples of good cooperation are based on individual interaction.

Industry does contract with research institutes to pursue new developments. This seems to be a stronger linkage with industry than is the case of university interaction.

Major applied research focuses on environmental needs and the recovery of metals from intermediate products from smelters and hydrometallurgical processes.

Table 5.4
Research in Institutes and Government Laboratories Pertaining to Hydrometallurgical Separation

UNIVERSITY, INSTITUTE OR LABORATORY	TYPE OF RESEARCH
Agency of Industrial Science and Technology (MITI)	Manganese nodule mining Ultrafine grinding Underwater rare metal extraction SX precious metals SX rare metals
Shizuoka University, Dept. of Applied Chemistry	SX tin, Cu(II), rhenium, moly, Al(III)
Saga University, Depts. of Applied Chemistry and Industrial Chemistry	SX indium, Cu(II), kinetics, Co(II), Pb(II), Pd(II), Hg(II), Pd(II), Pt(II), IX, Co(I), Ni(II)
Osaka University, Depts. of Chem. Eng. and Material Sci. and Eng.	Leaching of Scheelite Bacterial leaching in membrane bio-reactors Recovery of Ga and V from fly ash SX Co in HC1 Solutions
Kyoto University, Dept. of Metallurgy	Thermodynamics of solutions Mass transfer in solutions Leaching of CU Liquid membrane sep'n of Uranium SX stripping of Fe(III) Phase Equilibria Leaching of Malachite, Cuprite, Galena, Covellite, Columbite, Tantalite, Chalcopyrite Solubility of Uranium sulfate in H_2SO_4 Zinc electrowinning Activities of water and solutes Conductivity of Acid Chloride solutions Thermodynamics of U solutions Thiourea extraction of Gold Cementation SX kinetics Continuous SX Electroless plating

UNIVERSITY, INSTITUTE OR LABORATORY	TYPE OF RESEARCH
Tohoku University, Research Center for New Resources (formerly Research Institute of Mineral Dressing and Metallurgy)	Rapid separation at low concentrations Removal of oil and emulsions from sea water Electrochemical refining Refining raw materials by assorted mechanical forces Extraction of metals from unutilized resources Supercritical liquid extraction (aqueous) Controlled charge of characteristics of colloids Simultaneous grinding and extraction
Government Industrial Research Institute, Tohoku (GIRIT) - Sendai	IX development of ion-specific resins Impregnated resin extraction of gold platinum series metal chlorides, gallium, indium, molybdenum, tungsten, scandium and rare earths
University of Tokyo, Institute of Industrial Science	Metals extraction Removal of chloride ion from sulfate solutions
National Institute of Resources and Environment	SX modelling of Cu(II) extraction

REFERENCES

Everest Consulting Associates. 1982. *The International Competitiveness of the U.S. Non-Ferrous Smelting Industry and the Clean Air Act.* Princeton Jct., NJ.

U.S. Congress, Office of Technology Assessment. 1988. *Copper: Technology and Competitiveness*, OTA-E-367. Washington, D.C.: U.S. Government Printing Office.

Ishikawa, O. 1985. "Atmospheric and aqueous pollution control technology in Japanese copper smelting plants." In *Extraction Metallurgy '85*, ed. A.G. Moncrieff, London: IMM.

Mineral Industry Surveys. "Copper in the United States, April 1988." Branch of Nonferrous Metals, Department of Interior, Bureau of Mines, Washington D.C., 20241.

Mineral Industry Surveys. "Zinc Industry in May 1988." Branch of Nonferrous Metals, Department of Interior, Bureau of Mines, Washington D.C., 20241.

Onazaki, A., K. Sato and S. Kuramochi. 1986. "Effect of some impurities on iron precipitation at the Iijima refinery." In *Iron Control in Hydrometallurgy*, eds. J. E. Dutrizac and A. J. Monhemius. Chapter 40: 742-752. New York: John Wiley and Sons.

Von Rupanack, A. 1986. "Hematite -- the solution to a disposal problem -- an example from the zinc industry." In *Iron Control in Hydrometallurgy*, eds. J. E. Dutrizac and A. J. Monhemius. Chapter 40: 730-741. New York: John Wiley and Sons.

PRECEDING PAGE BLANK NOT FILMED

CHAPTER 6

THE STATUS OF ION EXCHANGE MEMBRANE TECHNOLOGY

H. S. Muralidhara

INTRODUCTION

Ion exchange (IE) membranes are very closely related to ion exchange resins in terms of their functionality. Several combinations of polymer matrices and functional groups are possible to produce a variety of IE membranes. Ion exchange membranes can be classified as homogeneous and heterogeneous. Homogeneous membranes are produced by a polymerization of functional monomers, whereas the heterogeneous membranes are produced by the melting and pressing of dry resins (Strathmann 1992).

There are four types of IE membranes:

a) Cation exchange membranes, where negatively charged groups are fixed to a polymer;

b) Anion exchange membranes, where positively charged groups are fixed to a polymer;

c) Amphoteric; and

d) Bipolar.

IE membranes are normally produced from vinyl polymers using a specific type of backing fabric and additives. Cation exchange membranes are manufactured by reacting styrene and divinyl benzene, whereas the anionic membranes are composed of a copolymer of vinyl pyridine and divinyl benzene or chloromethyl styrene and divinyl benzene. The Paste Method is used to obtain the desired mechanical properties by mixing a powdery polymer with a vinyl polymer. Once the polymerization process is complete, the IE groups are incorporated onto the film. Sulfonic and quaternary ammonium groups are attached to the cation and anion exchange membranes respectively.

THE DESIRED PROPERTIES AND APPLICATIONS OF IE MEMBRANES

The desired properties of the IE membrane are:

a) High ion permselectivity,

b) Low electric resistance,

c) Lower diffusion coefficient of the electrolyte, and

d) Chemical and dimensional stability.

IE membranes are used in a variety of applications, as shown in Table 6.1. There are several types of IE membranes used in a variety of unit operations and a range of applications (Table 6.2).

ELECTRODIALYSIS (ED)

As shown in Table 6.2, IE membranes are exclusively used in the electrodialysis of seawater for desalination purposes. The other emerging applications of the membranes for ED are given in the discussion below.

Japan is one of the leaders in ED technology. The Japanese have been successful primarily due to their R&D efforts in IE membranes over a period of 40 years. For example, Tokuyama Soda Company, one of the leaders in this technology, began its research efforts in the early 1950s. ED technology is energy intensive and hence very expensive. In spite of the cost, the company continues its research efforts due to incentives from the Japanese government. The government encouraged ED technology in response to the lack of the large land area required by the competing solar evaporation process for the manufacture of salt from seawater. The government built the first salt production facility with ED technology at a capacity of 10,000 TPY in 1956. Some of the milestones achieved by Tokuyama Soda in ED technology are given in Table 6.3.

Table 6.1
Application of Ion Exchange Membranes

ELECTRODIALYSIS	Salt production from seawater
	Production of drinking water
	Treatment of galvanizing effluent
	Demineralization of whey, etc.
SEPARATOR FOR ELECTROLYSIS	Chlor-alkali process
	Organic synthesis (e.g., glyoxal from oxalic acid, etc.)
	Synthesis of highly pure tetramethylammonium hydroxide for electronics industry
	Separator for electro-coat deposition process, etc.
DIFFUSION DIALYSIS	Acid recovery from waste acids
	Alkali recovery from waste alkali, etc.
PERVAPORATION	Dehydration of alcohol-water mixtures

In Japan today, 100 percent of food grade salt is produced from sea water using ED technology. Approximately 1.38 million tons of salt are produced per year by using more than 500,000 square meters of installed membrane surface.

One of the limitations of IE membranes for electrodialysis is fouling and scaling of membranes, especially for anion exchange membranes. Fouling is caused by an anion. The anion is too small and hence drives into the membrane structure. Since its electrophoretic mobility is poor, the anion deposits on the membrane surface and totally blocks the transport for the membrane. Japanese technologies, however, have made major improvements in coming up with an antifouling layer, which improves membrane performance. Very recently, composite membranes composed of anionic exchange membrane and polypyrrole have been tested in labs. Evaluation of many such materials is underway.

Other emerging applications of ED are:

a) Potable water from brackish water,
b) Effluent treatment of waste,
c) Demineralization of cheese whey,
d) Desalting of amino-acids, and
e) Desalting of soya sauce.

The ED industry in Japan is dominated by three companies: Tokuyama Soda, Asahi Glass, and Asahi Chemicals.

Table 6.2
Examples of IE Membrane Applications in Various Unit Operations

MEMBRANE TYPE	UNIT OPERATION	APPLICATIONS
Monovalent Cationic Permselective	Electrodialysis	Seawater desalination NaCl production from seawater
Monovalent Anionic Permselective	Electrodialysis	NaCl production from seawater Seawater desalination
Hydrogen Ion Permselective	Electrodialysis	Concentration of acid from waste acid
Anion Exchange membrane	Diffusion Dialysis	Recovery of acid from waste acid
Bipolar	Water splitting	Decomposition of salt

DIFFUSION DIALYSIS (DD)

The other major application of IE membranes is in diffusion dialysis. No electric current is presently in this type of dialysis. This method is based on selective adsorption of an acid on an anionic membrane, and hence when the membrane is equilibrated with a mix solution of an acid and a neutral salt, the acid concentration increases and the acid selectively travels to the membrane. This method can be used to separate hydrogen ions from potassium ions. This is rather a new application. Some of the advantages of this method are significant energy savings, simple process flow, and relative ease of operation.

Table 6.3
Milestones of Research and Development of Ion Exchange Membranes and Their Applications in Tokuyama Soda Co., Ltd.
(Courtesy of Tokuyama Soda)

1950	Beginning of research on ion exchange membranes
1956	Construction of salt production pilot plant (10,000 ton/year)
1962	Establishment of manufacturing method of "NEOSEPTA" membrane (Paste Method)
1965	Beginning to supply salt-producing process by electrodialysis to edible salt manufacturers in Japan
1972	Completion of process conversion in salt production from salt field to electrodialysis method in Japan
1974	Beginning to study fluorocarbon ion exchange membrane for chlor-alkali process
1984	Development of ion sensors for diagnosis (Na^+, K^1 sensors)
1985	Completion of process conversion in chlor-alkali production by own technology (300,000 tpm NaOH/Y) in Tokuyama factory
1986	Supply of new type of energy saving salt-producing electrodialyzer (TSX-200)
1986	Construction of electrodialytic salt production and chlor-alkali membrane plant in Kuwait (50,000 ton/y as NaCl)
1989	Development of anion exchangeable hollow fiber membrane for pervaporation
1990	Beginning to study on chitosan membrane for pervaporation

DD is not used widely in Japan. However, Tokuyama Soda researchers feel confident that its uses will grow mainly because of the potential energy savings from the use of such a technology. They mentioned that this technology will have major implications in environmental areas as well.

ED CORE

The other potential application of IE membranes is in the ED CORE technology being developed in Japan. Conventionally plate and frame configurations are used for any applications using IE membranes. However, this configuration poses swelling problems, thus limiting the performance of the membranes. Based on forty years of experience, Tokuyama Soda has developed a new ionic exchange membrane configuration, ED CORE, for applications such as electro-deposition of coatings. The novelty of this system is the tubular configuration, which is a departure from the conventional flat sheets. The design is such that the natural swelling of the ion exchange membrane is not restricted. In ED CORE, membrane backing material swells along with the IE membrane to maintain a smooth, wrinkle-free surface that will not trap fine solid material. The typical tube diameter is about 5 cm, and the length is 4 m to 5 m. At present, this configuration is being tested at General Motors and Ford plants in the United States.

BIPOLAR MEMBRANES

This technology development is rather recent. The membranes are laminates of both cationic and anionic membranes. Tokuyama Soda has been conducting extensive testing for over two years for a variety of applications. Some of the projected applications of bipolar membranes are:

a. Recovery of treatment chemicals from pulp and paper industry,
b. Regeneration of ion exchange resins from power plants,
c. Recovery of waste acids, and
d. Production of alkali.

Tokuyama Soda indicated that the bipolar membrane technology will be ready for commercial applications in one year. Aqua Tech and WSI in the United States are also developing similar technology. The Aqua Tech technology is already commercialized. However, the Tokuyama Soda researchers feel that they have an edge because of their superior process knowledge.

CONCLUSIONS

1. Japan has over forty years of experience in the development and manufacture of ion exchange membranes.

2. Japanese technology is world class.

3. The Japanese have developed a broad spectrum of membranes for sale and internal use.

4. The main theme is use of these membranes in environmental applications.

5. ED CORE technology is indeed innovative.

6. Development of new spacer materials and adhesives has constantly provided reliability for Japan's membrane processes. This, combined with better manufacturing techniques, definitely makes the Japanese world leaders in this industry.

7. Some of the major R&D efforts in the next five to ten years in this area will be:

    a) Enhanced operable life of the membranes or new membranes for seawater applications beyond ten years.

    b) Membranes that can withstand higher temperatures under oxidizing atmospheres.

    c) Separation of enantiomers.

    d) Ion exchange membranes as sensors.

REFERENCES

Strathmann, H. 1992. "Ion Exchange Membranes." In *Membrane Handbook*, eds. W. S. Winston Ho and K. K. Sircar. Van Nostrand.

PRECEDING PAGE BLANK NOT FILMED

CHAPTER 7

OTHER METHODS OF SEPARATION

C. Judson King
H. S. Muralidhara

DEWATERING (PULP AND PAPER INDUSTRY)

Water removal accounts for a very large portion of industrial energy consumption. Dewatering operations can be divided into *concentration* and *drying* processes, which produce more concentrated aqueous solutions and dry solids, respectively. Often concentration processes precede drying processes, since concentration processes tend to be less expensive per unit quantity of water removed. Concentration is most often accomplished by evaporation. Freeze concentration and membrane processes, notably reverse osmosis, electrodialysis and ultrafiltration, are other alternatives. The membrane processes can be less energy-intensive.

The JTEC panel did not encounter major innovations in dewatering processes, *per se*, that is, in drying, evaporation, freeze concentration, reverse osmosis and ultrafiltration. The panel was, however, very favorably impressed by energy savings accomplished in the Japanese paper industry, which for the most part resulted from decreasing the energy needed for evaporating water.

Japan is the second largest paper producing country in the world behind the United States. Its pulp production ranks third in the world. The pulp and paper industry in Japan consumes about 30 million cubic meters of wood annually. Approximately 70 percent of Japanese land is covered by forests. Its timber inventory ranks seventh in the world. However, its timber resources are not adequate to meet the country's pulp and paper demand. The pulp and paper production capacities of selected countries (based on 1988 figures) are given in Table 7.1.

Dewatering or water removal is an important operation in the pulp and paper industry. Some important dewatering stages in a typical pulp and paper mill are thickening of pulp, sludge dewatering, and sheet drying. Pulp thickening is accomplished mostly through thickeners that are rotary vacuum filters. Pulp consistencies of 12 percent to 16 percent are normally achieved. Dewatering and thickening of pulp is mostly done after pulping and before pulp storage, bleachings, refining, and so forth. Brown stock washing, accomplished through displacement washing, can be considered a dewatering step. Another main utilization of dewatering is for waste sludge before the final disposal of sludge as landfill or by incineration. The objective is to obtain solids concentration of at least 40 percent to 45 percent. Horizontal belt washers, vacuum drum filters, and screw presses are mainly utilized. Sheet drying is normally done using steam heated rotary cylindrical dryers. Air drying is also used in some mills to dry market pulp.

Efficient dewatering could save significant energy during the operation of dewatering equipment in pulp and paper mills. Hence the pulp and paper industry is working to reduce its energy costs by using sophisticated equipment and technologies. The industry's goals are to make dewatering more efficient and to look for cheaper energy sources. Japan's Ishinomaki mill (Jujo Paper Co., Ltd.) is a good example of the efforts of the pulp and paper industry in this regard. The dewatering equipment and the technology used by the Jujo mill are similar to the standard dewatering equipment and technology used by the U.S. pulp and paper industry. However, from the energy point of view, dewatering is receiving increased attention, especially during pulp washing and sludge dewatering.

THE ISHINOMAKI MILL

Ishinomaki is located in the northeast corner of Japan. It is the largest publication-grade paper plant in the world. Its daily paper production is 2500 tons per day (TPD) and the annual turnover is $830 million. The plant is very modern, and has good process and environmental controls. When the JTEC panel visited the plant, there was no odor characteristic of pulp mills.

Pulping

The mill imports about 580,000 tons of wood (as bolts) per year from Australia, Canada, and the United States. The rest of the wood raw material required is procured from its own resources. The mills use the modern Kamyr continuous digesters for pulping. The Kamyr digesters are known for their modern extended pulping methods. The Kamyr pulping technology is not new to the United States.

Table 7.1
Pulp and Paper Production Capacities of Selected Countries
(1,000 metric tons per year)

COUNTRY	PULP	PAPER
Austria	1,545	3,001
Finland	9,335	9,095
France	2,475	6,550
West Germany	2,265	11,404
Norway	2,150	1,913
Portugal	1,403	833
Spain	1,558	3,534
Sweden	10,585	8,630
United Kingdom	445	4,676
Subtotal	31,761	49,636
Total Europe surveyed by FAO	38,959	69,760
Australia	1,240	1,935
New Zealand	1,462	823
Subtotal	2,702	2,758
Total Oceania surveyed by FAO	2,702	2,758
Canada	24,744	17,028
United States	55,837	73,719
Subtotal	80,581	90,747
Total North America surveyed by FAO	80,581	90,747
Japan	12,847	27,143
Total Asia surveyed by FAO	17,330	51,933
World total in this study	127,891	170,284
World total surveyed by FAO	160,174	242,570

(Source: Buongiorno and Lee, *TAPPI J.*, July 1990)

Energy

The Jujo mill is self-sufficient in its energy requirements. The black liquor generated during pulping is used for energy generation as well as for chemical recovery. This energy is about 35 percent of the mill's requirement. The rest of the energy is generated from coal (imported from Australia) and oil. The following is a distribution of energy generation in the mill based on its source.

Coal (from Australia)	60 percent
Black liquor (from pulping)	35 percent
Oil	5 percent

Some electric energy is still purchased by the mill. Electric energy cost is as high as 12 yen/kwhr. Out of the total power demand of 150,000 kw, the mill purchases 6,000 kw of electricity at standard rate and 62,000 kw at discount rate.

Environmental

The mill is not anticipating any new dioxin regulations by the government; current regulations are based on informal mechanisms. By contrast, U.S. dioxin regulations are strict. Europe and Canada have the strictest dioxin controls in the world. However, the Jujo mill is moving towards chlorine-free bleaching to minimize the total organic halides (TOH) levels and thereby the dioxin problem. The Japan Environmental Agency (JEA) performed a large-scale investigation and concluded that the dioxin levels in the mill effluents are under control.

The environmental facilities at the mill are:

1. For effluent treatment (e.g., suspended solids, chemical oxygen demand, and color removal), five clarifiers, one of which is 106 meters in diameter, the largest of its kind in the world;

2. Two black liquor recovery boilers;

3. For sludge disposal, rotary kilns, screw presses and a sludge boiler;

4. Electrostatic precipitators (six for recovery boilers, two for pulverized coal boilers, and one for KP lime kilns);

5. Six scrubbers, five multicyclones and six sets of desulfurization equipment; and

6. For noise abatement, silencers and soundproofed walls.

THE JAPANESE PULP AND PAPER INDUSTRY

Figure 7.1 shows the trend in normalized purchased energy costs per ton of paper and paperboard output for the Japanese paper industry as a whole. This and the ensuing figures were supplied by Jujo Paper Company. Purchased energy per ton in 1990 was half that in 1975, the high year. In 1980 purchased energy accounted for nearly 20 percent of the total production cost of paper and paperboard in Japan, whereas by 1990 the portion of total cost attributable to purchased energy had dropped to about 8 percent (Fig. 7.2). By contrast, 50 percent of the total cost is for raw materials, and 35 percent is for chemicals.

This striking reduction has been achieved in five ways, none of which result from novel separations technology:

1. Extensive use of recycling
2. More energy obtained internally from the recovery plant, by virtue of obtaining a higher concentration of black liquor
3. Use of high-temperature, high-pressure boilers
4. Growth in production capacity at about 5 percent to 6 percent per year (New equipment is more energy-efficient)
5. Conversion to continuous digesters (Finnish technology), which are more efficient

It was pointed out that intense competition in the Japanese paper industry gives strong incentive to lower costs, through methods such as conservation of energy and make-up chemicals. In addition, as shown in Figure 7.3, there has been a trend toward deriving energy from coal, rather than oil. This probably reflects Japan's growing utilization of Australian brown coal. In addition, a growing fraction of electric power used in the Japanese industry is self-generated, having risen to about 66 percent in 1990 (Fig. 7.4.). This figure is 85 percent for Jujo Paper; its large Ishinomaki plant is self-sufficient with regard to electric power.

As is shown in Figure 7.5, a greater portion of the total energy consumed in the pulp and paper industry is self-generated in the United States than in Japan; however, the total energy usage per ton is greater in the United States.

Our Jujo Paper hosts cited figures to the effect that the United States has about 2.5 times the paper production output of Japan, but consumes 4.7 times as much purchased energy in doing so (Fig. 7.5).

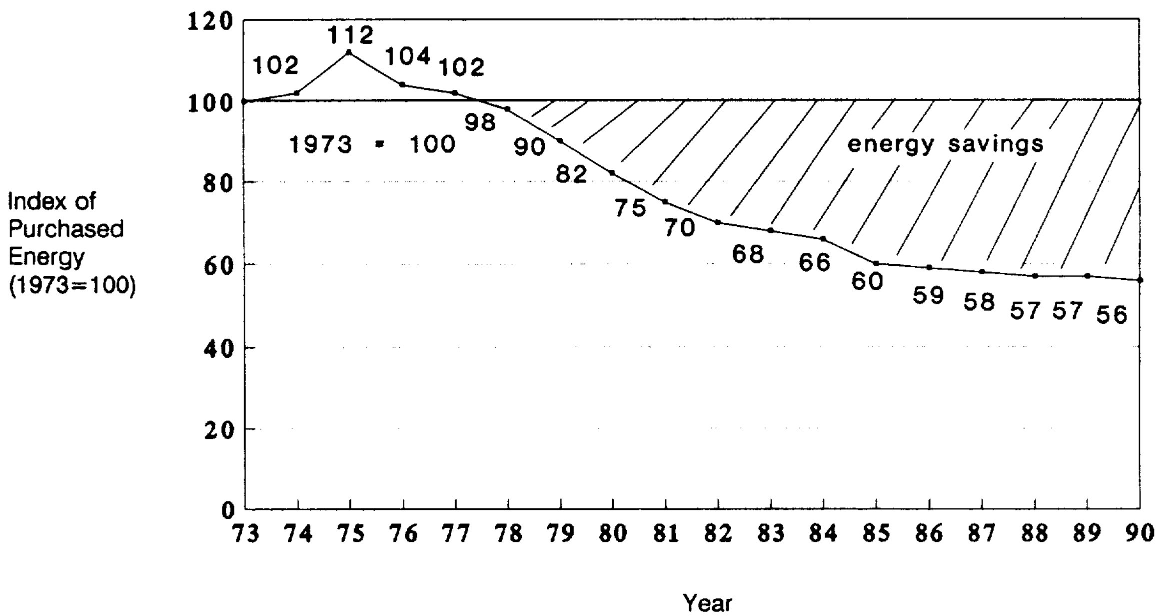


Figure 7.1. Trends in the Purchased Energy Per Ton of Paper and Paperboard Production

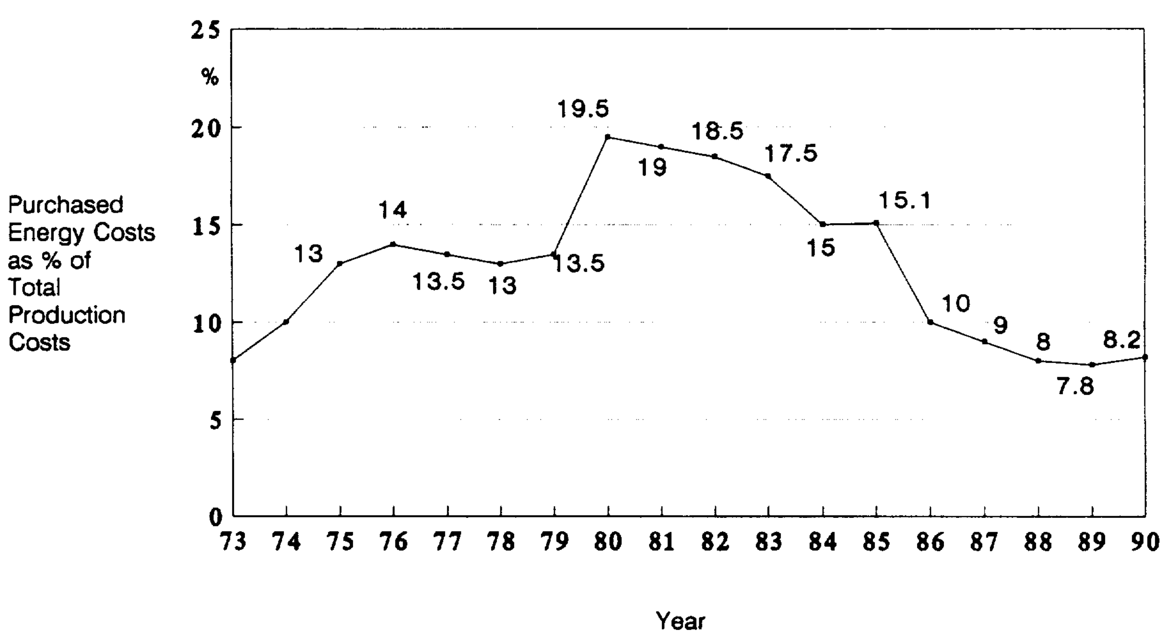


Figure 7.2. Trends in the Share of Purchased Energy Cost to the Total Production Cost of Paper and Paperboard

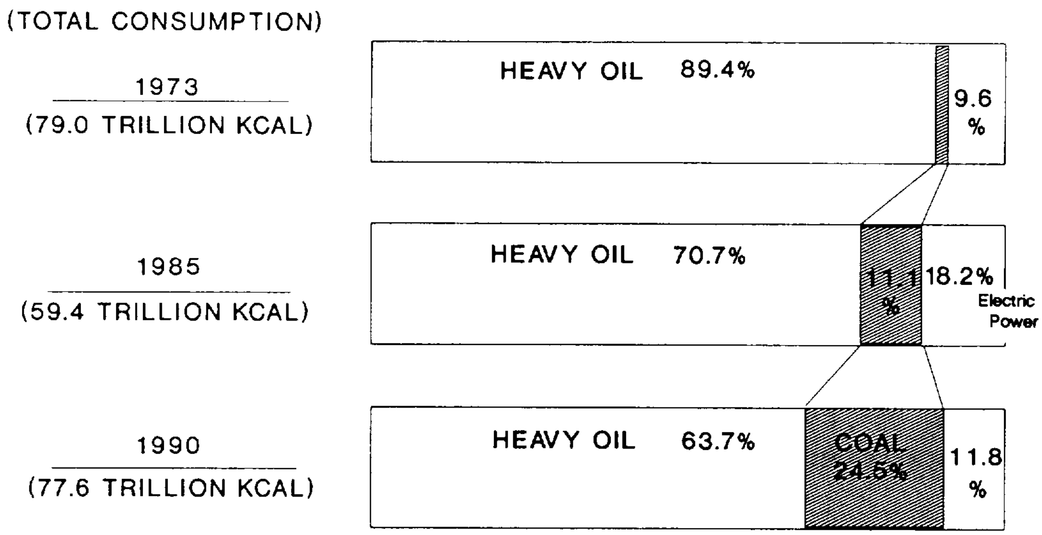


Figure 7.3. Trends in the Purchased Energy Sources of the Pulp and Paper Industry

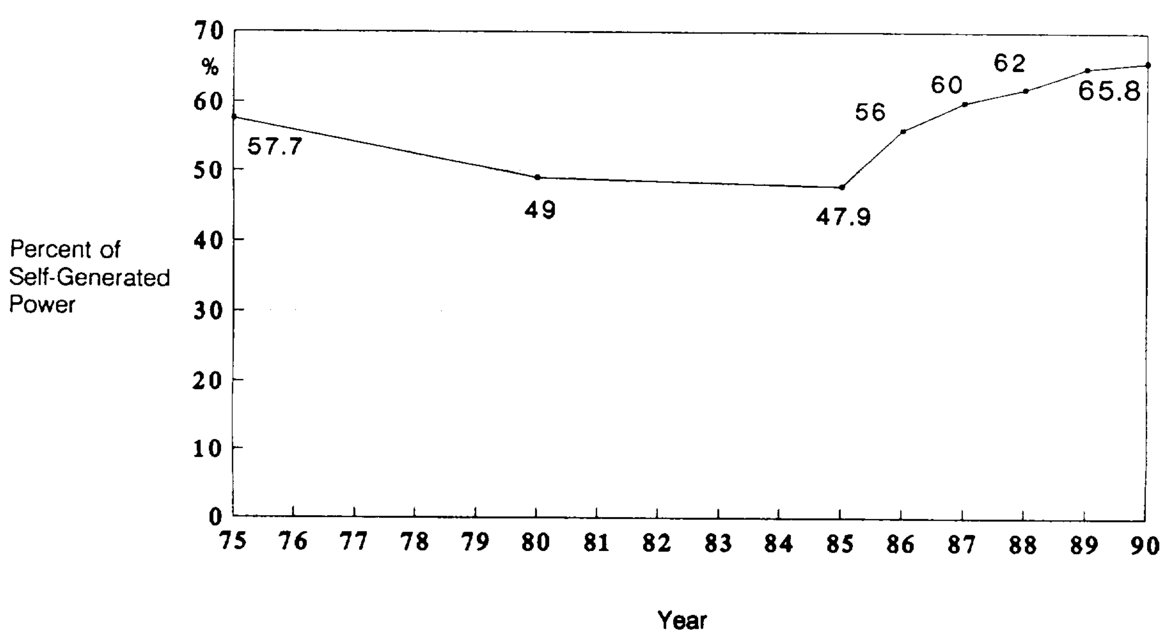
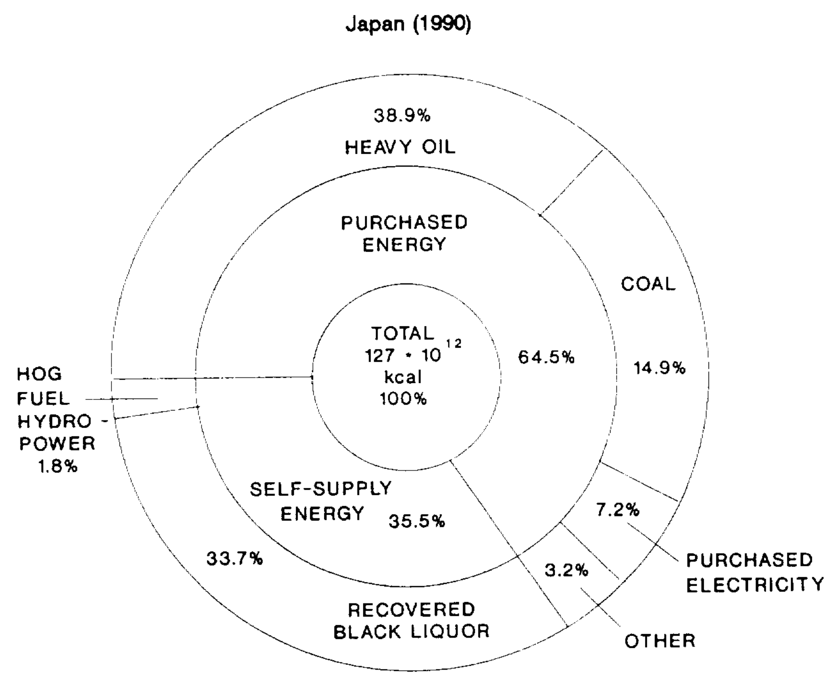


Figure 7.4. Trends in the Share of Self-Generated Power



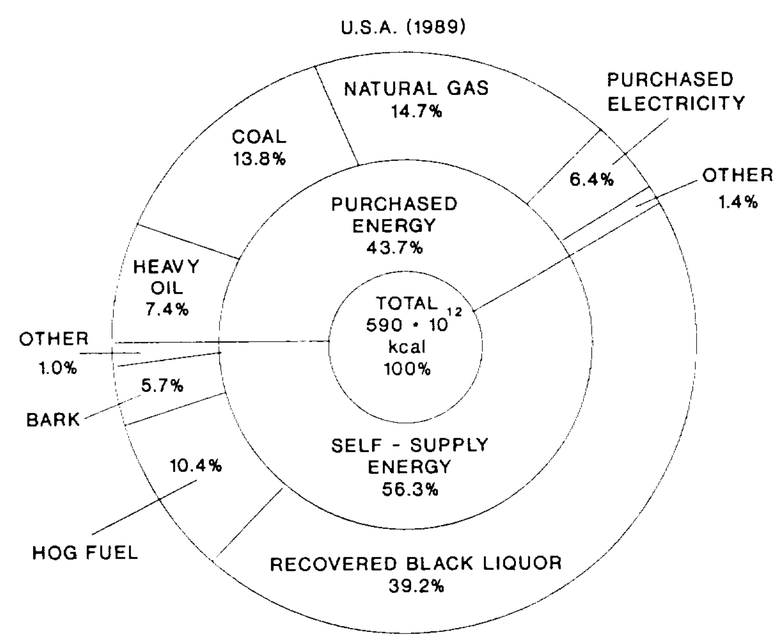


Figure 7.5. Energy Consumption/Sources in the Pulp and Paper Industry - Japan Compared to U.S.

It was further indicated that quality control is receiving increased emphasis in the Japanese pulp and paper industry; this is pushing energy consumption back upwards to some extent.

CRYSTALLIZATION

Crystallization is used for the recovery of sparingly soluble organics and inorganic salts, ranging from sugar to pharmaceutical products to table salt. It is an old and well-established process. Worldwide, research tends to be mostly in the academic sector, and has been heavily directed toward issues such as factors governing crystal-size distribution and crystal habit (morphology). Technological innovations have been infrequent.

The panel did, however, encounter a striking technological innovation in crystallization at Kobe Steel. Whereas the common approaches to crystallization produce supersaturation by evaporation of solvent and/or lowering temperature, Kobe uses a different driving force, namely an increase in pressure. For most mixtures, increasing pressure favors formation of a solid phase; water is an exception. This approach enables formation of solid phases that are stable at high pressure but unstable at atmospheric pressure. One can also alter eutectic compositions and compositions of solid intermolecular compounds. Dendritic growth and secondary nucleation can be avoided. Furthermore, application of pressure serves to force mother liquor to drain from the crystal bed. Pressure reduction brings about melting, and the amount of melting can be controlled through control of pressure. Partial melting serves to reduce surface irregularities through sweating, leading to more nearly perfect crystals.

REFERENCES

Buongiorno, J. and M. Lee. 1990. "International Forecast of Pulp and Paper Production Capacity: Accuracy of Alternative Methods." *Technical Association of Pulp and Paper Industries Journal (TAPPI J.).* July 1990: 106-114.

APPENDICES

APPENDIX A PROFESSIONAL EXPERIENCE OF PANEL MEMBERS

C. Judson King, Panel Chair

C. Judson King is provost for the Professional Schools and Colleges, and professor of chemical engineering at the University of California, Berkeley. He is the author of 2 books, over 200 publications, and 11 patents dealing with separations in general and extraction, adsorption, drying, and concentration processes in particular. He is a member of the National Academy of Engineering, and has received the Warren K. Lewis, William H. Walker, Clarence Berhold, and Food, Pharmaceutical and Bioengineering Awards of the American Institute of Chemical Engineers, as well as the George Westinghouse Award of the American Society for Engineering Education and the Mac Pruitt Award of the Council for Chemical Research. He chaired the National Research Council study entitled, *Separation and Purification: Critical Needs and Opportunities* (1987).

Edward L. Cussler

Edward Cussler is currently professor of chemical engineering at the University of Minnesota. He has a B.S. degree (cum laude) from Yale University, and M.S. and Ph.D. degrees from the University of Wisconsin, all in chemical engineering. He previously taught at Yale and at Carnegie Mellon universities, joining the University of Minnesota in 1980. A director of the American Institute of Chemical Engineers, Dr. Cussler is an authority on nonconventional separation processes. The author of 3 books and 150 papers, he is currently working on hollow fiber membrane separations and on microporous adsorbents. Recent publications discuss studies of ammonia selective membranes, efficient separation of racemic amino acids, hollow fiber gas drying, and hydrogeis as extraction solvents. In addition, Professor Cussler is the winner of many awards for teaching, and is an accomplished speaker on topics such as diffusion, hollow fibers as substitutes for packed towers, and ammonia selective membranes.

William Eykamp

William Eykamp is a consultant in membrane separations, currently based in Arlington, Massachusetts. Prior to that, he served as a visiting professor of engineering at the University of California at Berkeley. There he taught graduate seminars in the management of innovation (joint program between the College of Engineering and the Haas School of Business) and in membrane separations processes in the College of Chemistry. Previous to that he was President of Koch Membrane Systems (formerly Abcor, Inc.) after a series of positions in research and general management. His business activities included directorships in Japanese and European subsidiaries. His technical involvement in membranes includes pioneering the industrial uses of ultrafiltration, as well as the design of much of the successful early generations of ultrafiltration (UF) equipment. He was the principal investigator for the Department of Energy report on membranes separations (1990). Prior to his involvement with membranes, he worked in polymerization processes and in composite barrier materials. He earned his Ph.D. in chemical engineering from the Massachusetts Institute of Technology.

George E. Keller II

George E. Keller II is a senior corporate research fellow, Union Carbide Corporation. He is also manager of the Separations and Process Fundamentals Group, Central Research and Engineering Technology Department, at the South Charleston, West Virginia, Technical Center.

Dr. Keller received his Ph.D. in chemical engineering from the Pennsylvania State University. He joined Union Carbide in 1961. Since then he has been involved with a wide variety of projects involving both separations and reaction engineering. He presently oversees a portfolio of research and development activities in vapor-liquid and liquid-liquid separations, as well as in adsorption and membrane-based separations. From this group have come a large number of commercialized separation processes and process improvements. Two of these processes resulted in Kirkpatrick Honor Awards (second-place awards) for the top commercialized chemical engineering technology in the world.

Dr. Keller was elected to the United States National Academy of Engineering in 1988. In 1985 he received the American Institute of Chemical Engineers' Institute Lecture Award, and in 1990 he received *Chemical Engineering* magazine's Outstanding Personal Achievement Award. He has chaired two international meetings in separation technology and has lectured at over twenty universities in the United States and abroad. He currently serves on review committees at four major U.S. universities.

H. S. Muralidhara

H. S. Muralidhara is currently manager of the Process Technology Group at Cargill, Inc. Central Research. He specializes in separations technology research and is actively engaged in development of innovative dewatering technologies, applications of membrane technologies, and membrane fouling research. Dr. Muralidhara is coinventor of the electro-acoustic dewatering technology, which won the illustrious IR-100 award. Prior to joining Cargill, he worked at Battelle Memorial Institute (1981-1990) as a research leader. He was responsible for leading Battelle's research in the area of combined fields separation.

He holds a Ph.D. in chemical engineering from West Virginia University, an M.S. degree in thermal and environmental engineering from Southern Illinois University, and an M.S. degree in chemistry and chemical technology from India.

Dr. Muralidhara has edited two books on advances in solid/liquid separation and holds several U.S. patents in the area of separations technology. He is a member of the American Institute of Chemical Engineers and the Filtration Society. He also serves on the board of the *Separations Technology Journal* and the *International Drying Technology Journal.*

Milton E. Wadsworth

Milton E. Wadsworth is Distinguished Professor of Metallurgy at the University of Utah and served as Dean of the College of Mines and Earth Sciences for eight years (1983-1991). He received his Ph.D. from the University of Utah in 1951, and has been teaching at the university since then. His main areas of interest include surface chemistry of mineral systems, hydrometallurgy, mineral processing, and the kinetics of extractive metallurgy processes.

Dr. Wadsworth is past president of the Minerals, Metals and Materials Society (TMS) of the American Institute of Mining, Metallurgical and Petroleum Engineers (AIME), and is a member of the Society of Mining, Metallurgy and Exploration (SME), AIME, CIM, the American Society for Metals (ASM), the American Chemical Society, and the Electrochemical Society. He is a fellow of TMS and ASM, and a distinguished member of SME. In 1979 he was elected to the National Academy of Engineering. He was the 1991 president of AIME.

In December 1979, Dr. Wadsworth received an honorary degree "Honoris Causa" from the University of Liege, Belgium. In 1990 he received the honorary degree "Doctor of Engineering," from the Colorado School of Mines. He has received several honors, including four best paper awards in extractive metallurgy (two by

TMS and two Taggart Awards by SME), the James Douglas Gold Metal award of AIME, the Distinguished Teaching and Distinguished Research Awards offered by the University of Utah, the Minerals Industry Education Award of AIME, the A.M. Gaudin Award of SME, and the American Chemical Society Utah Award. He received the University of Utah Rosenblatt Prize and the Governor of Utah's Medal for Science and Technology. In 1989 Dr. Wadsworth received the Outstanding Educator Award of TMS.

APPENDIX B. SITE REPORTS - MEMBRANE COMPANIES

Site:	**Tokuyama Soda Co., Ltd.** **Tokuyama** **c/o Shibuya Konno Bldg.** **3-1, Shibuya 3-chome** **Shibuya-Ku, Tokyo 150, Japan**
Date Visited:	June 8, 1992
Report Author:	G. E. Keller

ATTENDEES

JTEC:

W. Eykamp
G. Keller
C. J. King

Hosts:

Yasuji Kida	General Manager, Tokuyama Research Laboratory
Koichi Doi	General Manager, Special Equipment and Chemicals Department
Ryuzi Izuo	Manager, Special Equipment and Chemicals Dept.
Fumio Hanada	Manager, Special Equipment and Chemicals Dept.
Yoshiaki Noma	Chief Engineer, Special Equipment and Chemicals Department
Atsushi Tomita	Chief Engineer, Special Equipment and Chemicals Department
Nobuhiko Ohmura	Research Chemist, Tokuyama Research Laboratory
Yoshinori Matsunaga	Assistant Manager, Special Equipment and Chemicals Department

BACKGROUND

Tokuyama Soda, Ltd. (TS) is a large ($1.2 billion sales in 1991), integrated manufacturer of basic inorganic chemicals and materials, petrochemicals, polymers, ceramics, and a wide variety of specialty products for the biomedical and personal care markets as well as other markets. In addition, there is a growing business in the sale of separation processes and process components ($16 million to $24 million per year).

TS has four main laboratories plus two smaller, more specialized technical centers. The team visited the Technical Research Laboratory in Tokuyama, where most of the research and development in separations is carried out. The mission of this laboratory is to understand basic technologies and to do development work in support of the Chemical Business Division and the Specialty Products Division.

Most of the separations research and development work is on membranes. Ion-exchange membrane research began in 1950. This work was spawned by the company's desire to produce salt from seawater to provide a self-sufficient supply for its caustic-chlorine process. By 1956, TS commenced construction of a salt-from-seawater plant, and in 1972 all of the solar evaporation capacity was replaced completely with electrodialysis to concentrate the salt from 3 percent in the seawater to 20 percent. Since then, research and development have continued on ED membrane development, as well as on a variety of new-membrane-process areas.

TECHNICAL DETAILS AND OBSERVATIONS

Areas discussed below include ED, diffusion dialysis, ED CORE, bipolar membranes, and pervaporation.

Electrodialysis

TS's work in this area has been quite extensive and has resulted in a number of specialized membranes that are sold under the trade name of NEOSEPTA. A major use is in the production of table salt. The company has commercialized this technology both in its domestic plant and in a plant in Kuwait. The Kuwait plant is a combined salt-plus-caustic-and-chlorine plant. There seem to be two reasons for salt production using ED in Japan: the lack of land area for solar ponds for evaporation/concentration, and the desire for at least partial national self-sufficiency in salt production. Salt production using ED is also used in Korea and Taiwan, but this route would not be the most economic choice in most other countries, including in the United States.

NEOSEPTA membranes, which are generally made in a flat-sheet form, have excellent electrochemical and diffusion properties, as well as mechanical and dimensional-stability properties. Membranes can be made with cation-exchange and anion-exchange properties, and can include both properties in one membrane. Both cation-exchange and anion-exchange membranes are made that are permselective for monovalent ions compared to higher-valent ions.

NEOSEPTA membranes have additional uses in the treatment of galvanizing effluent, for water purification, for desalting of amino acid mother liquor, for desalting of various food products such as soy sauce and sugar solutions, and for the demineralization of whey. Thus a major focus for these membranes is the reduction of waste loads and the recovery of useful products from streams that otherwise would have to be sewered.

Diffusion Dialysis

No electric current is present in this type of dialysis. One form of the membrane is permselective for hydrogen ions, and therefore will permeate acids, but not for other cations, and therefore will not permeate salts. Thus this membrane can be used to upgrade waste acids from pickling operations, to refine waste battery acid and to recover acids from various metal-refining operations. In some cases, at least, the percent recovery of acid can be greater than 90 percent. A second membrane is permselective for hydroxyl ion but not other anions. This membrane can be used to recover waste caustic from various salts.

Diffusion dialysis is not used widely today, but TS researchers feel confident that its use will grow. In all probability, the need to reduce pollution costs will be a factor in promoting the increased use of diffusion dialysis.

ED CORE

In the cathodic electrodeposition of paint onto car bodies, for example, anions must be conducted away from the car body and toward an anode. TS has developed a tubular anion-exchange membrane tube that surrounds a cylindrical anode. The tube diameter is about 5 cm, and the length is from 1 m to 4 m. Several such anode-plus-membrane combinations are used in a typical electrodeposition bath. Use of a cylindrical membrane eliminates several problems associated with flat-sheet membranes, such as swelling, wrinkling, and fouling. ED CORE is presently being tested in General Motors and Ford plants in the United States.

A second form of ED CORE uses a tubular cation-exchange membrane that surrounds a cathode. This arrangement is used in anion electrodeposition. This technology is now undergoing a field test, and TS researchers expect that it will be introduced to the market soon.

Bipolar Membranes

Bipolar or water-splitting membranes are a relatively recent addition to the TS research portfolio. The membranes contain both cationic and anionic functionalities on the same sheet. TS has tested its membrane in a water-splitting cell for over one year with stable performance. In addition, the company has under development a cell that produces caustic and sodium bisulfate from sodium sulfate and water. Uses for bipolar membranes are projected for recovery of treatment chemicals in the pulp and paper industry, for regeneration of ion-exchange resins in power plants, and for recovery of various acids from fermentation-reactor effluents.

TS researchers feel that their bipolar membrane technology will be ready for marketing in about one year.

Allied Signal in the United States also offers bipolar membranes. TS researchers feel that they have an edge based on superior process knowledge compared to Allied Signal.

Pervaporation

Pervaporation is another relatively recent (about 1989) addition to the TS membrane portfolio. The company has developed a hollow-fiber-based process for concentrating isopropanol in water from about 88 percent to 97 percent alcohol. The fibers appear to be somewhat under one millimeter in diameter, and are mounted as straight tubes in a bundle. Units are sold primarily to the electronics industry and for use in clean rooms. These units consist of both distillation and pervaporation steps to produce a high-quality product for recycle. Feed rates range from about 1 to 150 liters per hour. The fiber, whose composition was not revealed, has a selectivity for water over isopropanol of 100 or more. Research is presently centered on a new membrane using chitosan. This membrane is projected to have a selectivity of about 2,400, which could produce an isopropanol product of well over 99 percent.

CONCLUSIONS

TS's ion-exchange membrane technology appears to be world class. TS has a broad spectrum of membranes and processes available for sale and for internal use. A key theme for the use of these membranes is the reduction of waste-disposal problems. These membranes can be used for acid recovery, selective recovery of various metal salts and cleanup and reuse of water, as well as for a number of uses associated with the purification and upgrading of foods. Apparently there are commercialized units for many of these membranes.

The ED CORE technology is just getting started, and the size of the market for it is not yet clear.

TS's pervaporation technology seems suited for rather small installations. There was no indication that the process could be scaled to compete economically for large-chemical-plant applications. TS researchers do appear to be on the right track in developing a more economical capillary-tube (or hollow-fiber) technology for pervaporation rather than opting for the older plate-and-frame technology.

C-2.

Site: **Toray Industries, Inc.**
Shiga Plant
Toray Industries, Inc.
2-1, Sonoyama 3-chome
Otsu, Shiga 520, Japan

Date Visited: June 10, 1992

Report Author: E. Cussler
H. Muralidhara

ATTENDEES

JTEC:

E. Cussler
W. Eykamp
H. Muralidhara

Hosts:

Dr. Masaru Kurihara	Manager, Polymers Research Laboratories and Global Environment Research Laboratory
Dr. Yoshishige Fujii	Chief Research Associate
Dr. Toshio Yoshioka	Research Associate
Mr. Hiroyasu Kato	Research Associate
Mr. Hiroyuki Yamamura	Research Associate
Dr. Akira Ishitani	Vice President, Toray Research Center

BACKGROUND

Toray is a diversified company involved in the manufacture of a variety of polymeric materials, including fibers and textiles, plastics, films and film products, chemicals, high performance membranes, and electronic and imaging materials. The total annual R&D expenditures for the year ending March 1991 were ¥30 billion. Of this, 26 percent was spent for corporate research.

Toray divides its businesses into three main sectors: fibers and textiles, plastics and chemicals, and new products and other businesses. High performance membranes and related equipment belong in the latter category.

Dr. M. Kurihara gave an excellent presentation on the status of membrane technology at Toray. He categorized the company's membranes as:

Advanced reverse osmosis (RO) membranes:

> Low pressure UTC-70
> Ultra-low pressure UTC-60
> Desalination membrane UTC-80
> Ultrapure water membrane UTC-90

Advanced liquid separation membranes:

> Thermally sterilizable, chemically stable, microfiltration (MF), UF

Gas/liquid separation membranes:

> Removal of dissolved gases and facilitating absorption of gas into liquids, especially during ultrapure water production.

During the presentation, Dr. Kurihara indicated that the performance of Toray's membranes was comparable to Dupont's A15 series or Filmtech's TW/BW/SW series. In the Toray UTC series, the dominant polymeric material is based on triamine.

Toray claims that performance of the low pressure UTC-70R type of membrane is slightly better than other commercially available composite RO membranes. The UTC-70R spiral wound membrane appears to have better than 99.7 percent rejection at 15 kg/cm^2 pressure, 25 °C, and 1500 parts per million (ppm) NaCl concentration. The company claims that it has improved its spiral-wound design, especially the spacer design, significantly, and hence has eliminated a number of problems such as bacterial growth on the permeate side, and so forth. Membrane materials currently manufactured by Toray and their applications are given in Table Toray.1.

Our hosts mentioned that 50 percent of Toray's membrane market is in ultrapure water production for the electronics industry. Toray's success appears to be due to the process integration the company has developed. The most intriguing aspect of its design is the degassing process. An example is provided in Figure Toray.1.

Toray is continually developing new membrane materials for a variety of applications. PPSS (Polyphenylene sulfide sulfone) and PPSO (Polyphenylene sulfone) membranes could make a significant impact in the petrochemical and in the oils and fats industries due to their solvent resistance and heat resistance capabilities, as well as large fluxes due to the spiral wound design. If this membrane is successful, it will open up a large market, since the membrane can be manufactured at a reasonable cost.

Table Toray.1
Membrane Materials Manufactured and Their Applications

MATERIAL TYPE	SERIES	APPLICATION
Asymmetric Cellulose Acetate	SC	Ultrapure water, medical use, boiler feed
Polyether Composite	SP	Desalination, drinking water
Cross-linked Polyamide Composite	SU	Concentration/recovery of high value products, desalinization of brackish water, ultrapure water
Polymethymethacrylate	B	Hemo-Dialysis, Hemo-Diafiltration

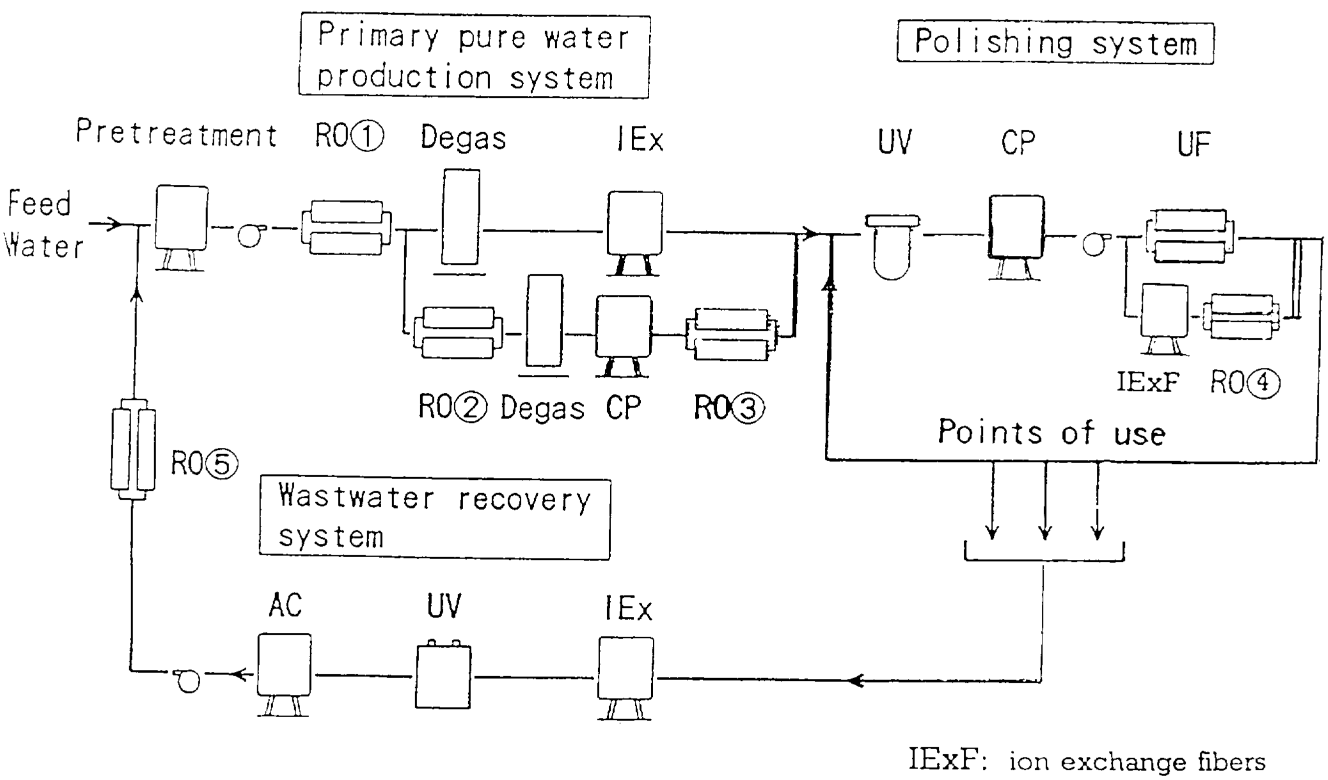


Figure Toray.1. Ultrapure Water Production System

IONEX

Toray's ion exchange fibers are based on polystyrene. These new products have been introduced into the market successfully due to Toray's unique composite fiber proprietary technology and software knowledge of polymer chemistry. The base polymer is polystyrene, and the reinforcing polymer is polyethylene.

Characteristics of Toray's fibers

- Good chemical stability
- Degree of cross-linking freely controllable
- Shape of fiber is 0.2 mm - 1 mm length as well as sheet form
- Surface area is 10 - 100 times higher than conventional ion exchange bead resin
- Excellent adsorption capacity to macromolecules, fine particles as well as microorganisms

Current Applications

- Production of ultrapure water
- Treatment of condensed water in nuclear power generators
- Immobilization of proteins
- Adsorption/separation of mutagenic components in cigarette smoke

Although the pressure drop is higher in this type of device compared to the conventional bead type, the uptake rates are much higher as well. At present, demonstration experiments are going on in the United States and Japan in nuclear power plants for treatment of condensate water.

DRUM FILTER

Toray has developed a continuous, advanced, drum-filtering concentrator concept containing a special fabric filter for separating ultrafine suspended solids from liquids. The filter consists of two layers -- a surface layer with an ultrafine fiber, and a sublayer consisting of an ordinary thin layer. Once the particles are deposited on the surface, they can be easily cleaned with a backwash water jet.

MEMBRANE CONTACTORS FOR DEGASSING

Toray sees four major markets for membrane contactors: boiler feeds, hemodialysis, ultrapure water, and soft drinks. All are commercial, though the last two are better developed.

Toray's system for membrane contactors uses a silicone composite membrane in a spiral wound module. Some modules collect the gas removed by drawing a vacuum on the central tube. Other, more efficient modules plug the central tube, and separate the membrane envelope with a glue line, running from the tube to near the end of the module. A sweep stream of nitrogen enters the end of the tube, spirals outward to the end of the glue line, rounds this glue line, and spirals back to the central tube. Modules with a sweep are typically twice as effective as modules run with vacuum alone.

The performance of the modules, characterized with an overall mass transfer coefficient times a total membrane area, cannot be completely analyzed from the fragmentary data given. These data suggest an area per volume around 30 cm^2/cm^3, though Toray's own analysis suggests a figure of approximately 8 cm^2/cm^3. The data supplied to the panel by Toray also appear to imply that about half the resistance to mass transfer comes from the nonporous silicone membrane. Neither of these values is especially good.

Toray has made these systems work commercially. Their performance is perhaps one fourth of that routinely produced by American-made contactors. Still, Toray has delivered working systems while these American manufacturers have dithered about further improvements. As a result, Toray's accomplishments command respect.

SUMMARY

Toray is undoubtedly one of the world leaders in membrane materials and technology. Its membranes perform equally well or better than those of other manufacturers, especially for RO applications. Toray's redesign of spiral wound elements and spacer material development is unique. If the company can develop a high-temperature resistant, solvent-resistant type of membrane successfully on a commercial scale, this could add a new dimension to the use of membranes in the petrochemical and oil and fat industries.

Site: **Nitto Denko Corporation**
61-7, Aza-Sasadani, Yamadera-cho
Kusatsu, Shiga 525, Japan

Date Visited: June 10, 1992

Report Author: H. Muralidhara
E. Cussler

ATTENDEES

JTEC:

E. Cussler
W. Eykamp
H. Muralidhara
B. Williams

Hosts:

Hiroshi Iwahori
Noriaki Yoshioka

BACKGROUND

Nitto Denko is one of the larger membrane companies in Japan. Nitto's product mix is somewhat similar to that of the 3M Company. Nitto Denko is also into tapes, microelectronic materials, chemicals, and bar codes. Nitto Denko representatives indicated that the company's membranes account for about 4 percent of its consolidated total sales, $75 million per year.

Nitto Denko manufactures a variety of membrane products, including spirals, hollow fibers, and tubulars. The main applications include reverse osmosis for ultrapure water production, ultrafiltration for treatment of food processing and wastewater effluents, and so forth. Membrane treatment for ultrapure water used in the electronics industry is apparently one of the company's large applications and has been very successful.

A video was shown that outlines some of Nitto's membrane manufacturing methods. It appeared that all the membranes, regardless of their application, are manufactured in a clean room environment. It seems that this may not be justifiable for an application such as in wastewater treatment. The company also indicated that the spiral-wound membranes are formed in place by using either epoxies or urethanes that are ultrafiltered. According to Nitto, manufacturing yield is more than 98 percent. Nitto is very proud of these results.

The JTEC visit to Nitto Denko documented Nitto's substantial commitment to quality in manufacturing to a great extent. The hosts for the Nitto visit were both managers of Nitto's membrane division. They stated that Nitto's membranes account for about 4 percent of Nitto's total sales, about $14 M/yr.

Membrane products manufactured by Nitto at the Shiga Plant include hollow fibers, spirals, and tubular membranes, almost all of which relate to liquid separation membranes. These membranes are largely used for reverse osmosis and ultrafiltration. Therefore the discussion during this site visit was limited to water separation membrane technology. Pervaporation and gas separation are occasionally mentioned in Nitto's brochures. Although gas separation membrane technology was discussed briefly during the site visit, our hosts stated that Nitto Denko was currently focusing on an application of organic vapor separation, the plant system of which was being jointly developed with another Japanese company. However, there was no opportunity to discuss the status of Nitto's organic vapor separation membrane in depth during the JTEC site visit.

Battery separators, another Nitto product from a different part of the company, are a minor effort. Bioreactors, a past focus, are not now an active topic. Hollow fibers, especially for ultrafiltration of ultrapure water, seemed to be an important topic, and were discussed extensively during the JTEC site visit. They account for about 30 percent of the membrane division's sales. The chief competition was said to be Asahi Chemical; Toray was not mentioned. Ultrapure water for the microelectronics industry is made by processes like that shown in Figure Nitto.1. This process seems similar to those suggested by other companies. Ultrapure water can also be used for pharmaceuticals, especially for injectables.

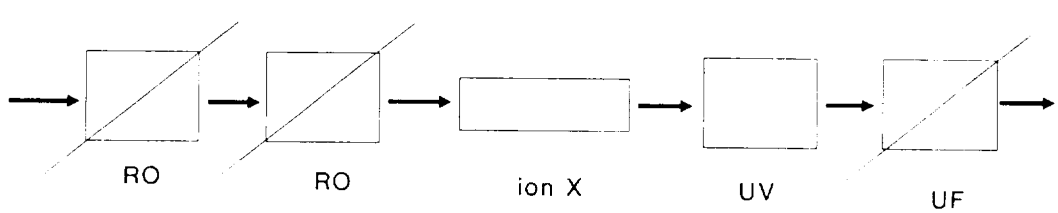


Figure Nitto.1. The Basic Ultrapure Water System. Most commercial systems include additional steps beyond this basic system; some employ recycles of used water.

Hollow fiber membranes are made from polysulfone with inside diameters of 550, 700, and 1100 μm, with thicknesses ranging from 225 to 400 μm, respectively. In a scanning electron microscope (SEM) photo, these membranes show an asymmetric double skin layer structure, with slightly loose pores in the outer core. They are used in an internal pressure mode, with the exception of the 700 μm inside diameter fiber, which has been released recently for use in an external pressurizing-type module intended for the production of ultrapure water for 16 megabit VLSI memory chip production. The 550 μm inside diameter fibers are coated on the inside, apparently by an interfacial polymerization. Modules are made by forcing epoxy resin into the ends of the module by centrifugal force. Excess epoxy compound is trimmed while the module is hot (<98°C). After trimming, the cut ends of the module are coated with an extra layer of epoxy to prevent leakage through the support layer without crossing the skin layer surface. In the most advanced ultrapure water systems, these fibers in the external pressurizing module are fed on the shell side; the permeate contacts only the internal skin layer surface, which can minimize the secondary contamination by particles coming from the module's component materials. While this would seem to increase concentration polarization, it is said to reduce fouling and facilitate cleaning by backmixing. Scattered data support this.

Spiral wound modules for reverse osmosis, which is Nitto's major business, are also well developed. While no membrane chemistry was described, one of the systems in use by Nitto presumably is close to Filmtec's patented membranes, since Hydranautics (Nitto's U.S. subsidiary) is forbidden by court order to sell the CPA2 membrane in the United States. As a result, Nitto makes several types of composite membranes in Japan and the United States; depending on the membrane type, they are assembled into modules by Hydranautics or by Nitto's Mexican subsidiary. Nitto then sells these modules on the world market.

While some of Nitto's membrane chemistry for these reverse osmosis modules may be derivative, the company's membrane manufacturing technology seems exceptionally good. The team did not see this directly, but did see a somewhat superficial video outlining these ideas. The video shows extremely careful manufacturing at every step. Membranes are formed by interfacial polymerization on a web. The membranes are formed into spirals using epoxies or urethanes. All workers pass through air showers to work under near-clean room conditions. These precautions lead to a 2 percent rejection rate in finished modules, or as Nitto Denko describes it, a 98 percent yield.

The Nitto group has installed major reverse osmosis and ultrafiltration plants, including ones in Yuma, AZ, Fort Myers, FL, and at IBM in New York. These installations, which may not depend on the best membranes available, are installed by Hydranautics, located in San Diego. This group seems to be an accomplished designer of membrane systems. The JTEC team did not have an opportunity to discuss Nitto's research ideas during its brief visit.

SUMMARY

Nitto Denko is one of the leading membrane companies in Japan. The company has excellent quality manufacturing methods. The panel did not have an opportunity to see any especially innovative developments taking place at Nitto, and therefore cannot say whether there are any such developments underway.

Site: **Asahi Chemical Industry Co., Ltd. (Asahi Kasei)**
Fuji City, Shizuoka-Ken
c/o Industrial Membranes Division
1-1-1 Uchisaiwai-cho
Chiyoda 100, Japan

Date Visited: June 11, 1992

Report Author: G. Keller

ATTENDEES

JTEC:

E. Cussler
W. Eykamp
G. Keller

Hosts:

Yoshikazu Inai	General Manager, Industrial Membranes Division
Yoshiaki Kuwada	Plant Manager, Fuji Industrial Membranes Plant
Kohei Watanabe	General Manager of R&D Division, Fuji Industrial Membranes Plant
Hirokazu Ohno	Assistant Manager of R&D Division, Fuji Industrial Membranes Plant
Charles H. Chayamichi	General Manager, Overseas Operation, Industrial Membranes Division
Koichi Matsumoto	General Manager of Technical Sales Overseas Fuji Industrial Membranes Plant

BACKGROUND

Asahi Chemical Industry Co., Ltd. (ACI) is a very large ($9.2 billion in sales in 1991) and diversified manufacturer of a wide range of chemicals and polymers, with products ranging from commodity products to specialty chemicals, materials and systems. Chemicals and plastics accounted for $3.5 billion in sales, housing and construction materials for $2.4 billion, fibers and textiles for $1.7 billion and special products and services $1.7 billion.

Asahi's membranes have found applications in many fields, including kidney dialysis, recovery of salt, manufacture of caustic and chlorine, recovery of automotive electrodeposition paints, production of ultrapure water for semiconductor manufacturing, refining and concentration of proteins and enzymes for pharmaceutical production and the production of pyrogen-free water. These membranes are the responsibility of several divisions. The Industrial Membranes Division, the plant and R&D facilities of which are located at Fuji City, is responsible for ultrafiltration and microfiltration membranes and processes using these membranes. It was this division that the team visited. Other divisions have responsibility for ion-exchange membranes, membranes for separation of viruses from blood plasma, and kidney-dialysis units.

Membrane research and development began in 1971, with hollow-fiber ultrafiltration membranes as the initial focus. Commercial production began in 1976, featuring a double-skin hollow fiber. (A year earlier a microporous, flat-sheet membrane for use as a battery separator was developed.) From the beginning, the emphases have been on selling systems, not just fibers, and on strong technical support for the customers. Most of these early systems found use in water purification. In 1982, further commercializations of hollow-fiber microfiltration membranes occurred, with primary uses in fermentation broth separation and dewaxing of edible oil.

TECHNICAL DETAILS AND OBSERVATIONS

Asahi membranes are made in ultrafiltration and microfiltration forms. All of these membranes consist of hollow tubes or fibers with outside diameters ranging from less than one to about three millimeters. Flow can be either from the inside out or from the outside in, depending on requirements of the process. The UF membranes have dense layers on both the inside and outside surfaces. These membranes are made from polyacrylonitrile and polysulfone. Polysulfone-based membranes have excellent thermal stability and can be steam-sterilized. This is an important consideration for use in the food and pharmaceutical industries. Very few other companies, according to Asahi researchers, can market a steam-sterilizable polymer membrane system.

MF membranes are made from polyolefins, polyvinylidenefluoride, and a hydrophilic polymer. These membranes in general have excellent chemical resistance to organics such as formaldehyde and sodium hypochlorite, which are used for chemical disinfection.

Module sizes can range from small lab scale to ones five inches in diameter. Flow to the latter is about 5,000 liters per hour.

Typical applications for these membranes are listed in Table Asahi.1.

A major area of interest for the Industrial Membranes Division is the production of ultrapure water for use in the electronics industry. As chips have become more and more densely packed, the requirements for water purity have risen (see Table Asahi.2). Asahi supplies UF membrane modules for use by others -- Kurita, for example -- for the final step in the overall processes for water ultrapurification. Asahi researchers feel that their membranes are compatible with the water-purity needs of the 16 megabit DRAM chip.

Table Asahi.1
Typical Applications

SEMICONDUCTOR INDUSTRY	Preparation of ultrapure water, particle removal from chemicals, recovery of water from the dicing machine and back-grinder coolants
PHARMACEUTICAL INDUSTRY	Preparation of purified water or water for injection, cell harvesting, protein concentration, purification of pharmaceuticals, endotoxin removal, plasma separation, vaccine production
AUTOMOBILE INDUSTRY	Recovery of electro-deposition paint
MACHINE INDUSTRY	Oil/water separation
FOOD INDUSTRY	Flocculus separation from sake (Japanese rice wine), bacteria removal, concentration of gelatin

A second major market for ultrapure water is in the medical area. The most stringent specifications are for what is called Water For Injection (WFI). Both membrane separation performance and sterilizability are important here. Presently WFI is made by distillation, but Asahi researchers feel confident that the market will shift to membranes. A typical unit might produce about five tons per day of WFI, part of which would be used for other somewhat lesser-quality water needs.

Asahi is well aware of the interest in improved batteries for electric cars, and the company is quite interested in doing research on battery membranes. The team could not tell the extent to which this research is presently underway.

Asahi's analytical-chemistry capabilities are truly world class. The company has a wide range of state-of-the-art spectroscopic and other equipment to analyze its membranes. The polymer science capabilities of the company also seem to be excellent.

Pall Corporation (United States) has signed an agreement with Asahi to market Asahi's UF membranes in the United States as well as in Europe and other areas.

Table Asahi.2
Chronological Change in Ultrapure Water Quality Requirements

Mass Production Timing	1984-	1987-	1990-	1993-
Dynamic RAM (bits)	256K	1M	4M	16M
Resistivity (MΩ x cm)	> 17.5	> 17.5-18.0	> 18.0	> 18.1-18.2
Particle Count (No./mℓ)				
> 0.20 μm	< 50			
> 0.10 μm		< 10-20	< 5	< 1
> 0.05 μm				< 5
Bacteria Count (cfu/ℓ)	< 100	< 10	< 5	< 1
TOC (μg/ℓ)	< 50-100	< 30-50	< 10-20	< 1-5
Silica (μg SiO_2/ℓ)	< 10	< 3-5	< 1-5	< 0.1-0.5
DO (μg O/ℓ)	< 100	< 50-100	< 20-30	< 5-10
Metal (μg/ℓ)		< 0.1-0.5	< 0.1	< 0.01-0.05

Asahi researchers believe that they are the largest supplier of membranes to the industrial market in Japan. They also feel that their membranes in most cases are superior to those of their competition. The JTEC team asked them which company's membranes were the best in various areas in Japan and in the United States. Their listing, given unofficially, is shown in Table Asahi.3.

CONCLUSIONS

Asahi is clearly a major force in industrial UF and MF in Japan, and its relationship with Pall Corporation should give it additional sales opportunities around the world. The polymer and analytical-chemistry infrastructure provided by the rest of the Asahi company will serve as an excellent resource for the Industrial Membrane Division's continuing improvement of its products. This continuous improvement will be necessary, because there appears to be intense competition among several companies in the UF and MF areas for what may be a limited amount of business. A major question would seem to be associated with the rate of growth of the business opportunities for UF and MF. Opening up of the WFI market to membranes would be a step in the right direction.

Table Asahi.3
Asahi's Informal Rating of Membrane Companies in Japan and the U.S.

AREA	JAPAN	U.S.
Gas separation membranes	None	?
Steam-sterilized polymer membranes	Asahi	?
Cation electrodialysis	Asahi	Koch
Ultrapure water production	Asahi	MF: Pall, Millipore UF: Romicon
Biotech separations: steam sterilization	Asahi	?
Biotech separations: fermentation broth	Asahi	Pall, Millipore
Desalination	Toray	DuPont, Dow
Water purification for households	Mitsubishi, Toray	None
Artificial kidney	Asahi	Enka (?)
Ion-exchange membranes	Asahi	Ionics (?)
Racemic separations	Daicel	?
Membrane separations in the food area	No big Japanese market	?

APPENDIX C. SITE REPORTS - OTHER COMPANIES

Site:	**Kobe Steel, Ltd.** **3-18 Wakinohamacho 1-chome** **Chuo-Ku, Kobe** **Hyogo 651, Japan**
Date Visited:	June 10, 1992
Report Author:	M. Wadsworth

ATTENDEES

JTEC:

G. Keller
C. J. King
G. Lim
H. McGee
M. Wadsworth

Hosts:

Dr. Yoshihiro Yamaguchi	Director, Technical Development Group
Dr. Masato Moritoki	New Business Division
Noboru Ikawa	

BACKGROUND

Kobe Steel is a highly diversified company in commodities, manufacturing and research. Its activities extend worldwide with over seventy subsidiaries, affiliates and investments in twenty countries. U.S. affiliates are U.S. Steel, Alcoa (aluminum in automobiles and cans) and Texas Instruments (semiconductors). The business divisions of the company are the Iron and Steel Division, the Welding Division, the Aluminum and Copper Division, the Engineering and Machinery Division, the Cutting Tool Division and the New Business Division. The Technical Development Group consists of the Materials Research Laboratory, the Mechanical Engineering Research Laboratory, the Polymer and Chemical Technology Laboratory, the Electronics Research Laboratory and the Biotechnology Laboratory.

The total research budget is 3.4 percent of total sales, including research in the parent company and all divisions. Separation technology is extant through all commodity divisions of the company, extending from steel and base metals to specialty materials and gases.

Of special interest are separation technologies based on high pressure, utilizing a long history of experience in the area by Kobe Steel. Specific new high-pressure, commercialized technologies are: 1) high-pressure crystallization and 2) supercritical fluid extraction.

TECHNICAL DETAILS AND OBSERVATIONS

High-Pressure Crystallization (Dr. Masato Moritoki)

At elevated pressure (> 2,000 bars), many organic compounds can be crystallized as a result of decreased solubility with increasing pressure. Steps in the process are carried out during a single pressure cycle and consist of:

1. crystallization by pressurization,
2. separation of mother liquor,
3. sweating and purification by partial release of the pressure, and
4. cake removal.

Since all steps are achieved during a single pressurizing/depressurizing cycle, the crystallization and purification steps can be completed in times measured in a very few minutes. The process is thus featured by short cycles with high yields (90+ percent of theoretical) and low energy consumption (mechanical only). Various applications fall in the temperature range of -10 to 60°C depending on the materials. One commercial unit consists of a 15-liter crystallizer with a cycle time of 4.5 minutes. This unit is operated over 8,000 hours per year.

In operation, the liquid is pre-cooled prior to introduction into the pressure chamber. This helps to compensate for the liberation of heat that occurs during crystallization. Examples given of application of this technology included purification of p-cresol, naphthalene, and other chemicals.

Supercritical Fluid Extraction (Noboru Ikawa)

This process, using high-pressure columns, has several unique applications. Batch processing is used for extraction of natural flavors and colorants from plants, and oligomers from polymers, as well as for recovery of pharmaceutical chemicals. In continuous processing applications, supercritical fluid extraction (SFE) is used for the extraction and/or enrichment of polyunsaturated fatty acid from fish and vegetable oils and for separation of ethanol from fermentation broths. Some of these processes have been commercialized.

A modification of the process is based on a combination of extraction and supercritical fluid chromatography. This process, which is under development for commercial use, has been used successfully for the separation of polyunsaturated fatty acid from vegetable and fish oils. A new effort has focused on SFE for ethanol concentration to replace conventional distillation and azeotropic distillation. This process is currently in the pilot-plant stage.

Gas Separation Technology

Though it was a relatively minor topic of conversation during the meeting, the Kobe Steel literature indicates that significant work has been done on developing and commercializing a number of gas separation processes. Air separation for both oxygen and nitrogen, hydrogen recovery and carbon monoxide recovery processes have been developed based on pressure-swing adsorption. These processes are available for licensing. In addition, Kobe Steel has licensed for its own use Tenneco's COSORB process for carbon monoxide recovery. In the environmental area, units for removal of SO_x, NO_x, H_2S (Stretford process), radioactive gases, and mercury are used. A honeycomb-type activated-carbon filter for decomposing ozone has been developed for sale.

Coal Conversion Technology

Kobe Steel is involved with a large project to convert coal from Australia to liquid fuels and chemicals. The team visited a large pilot facility in which coal was being catalytically hydrogenated in a two-step process, with the products subsequently being recovered. The separation technology appeared to be relatively conventional and consisted of an ash-removal step and distillation to separate the product into several refined streams.

CONCLUSIONS

The ability of Kobe Steel to develop innovative separation process technology is impressive. The chief inputs that Kobe Steel seems to use are its internal needs for separation technology and its ability to use certain aspects of the company's overall technology -- high-pressure know-how, for example -- to develop separation processes for sale outside of the company. Especially innovative is Kobe Steel's high-pressure crystallization process. A key factor in the economics of this process will be the capital cost of the equipment. The energy costs should be quite good.

In the gas separation area, the technology of Kobe Steel is probably much the same as that available from other companies.

Site: **Kurita Water Industries Ltd.**
Central Laboratories, Atsugi
c/o Research and Development Division
Kurita Water Industries, Ltd.
4-7 Nishi-Shinjuku 3-Chome
Shinjuku-ku, Tokyo 160 Japan

Date Visited: June 11, 1992

Report Author: W. Eykamp

ATTENDEES

JTEC:

E. Cussler
W. Eykamp
G. Keller
G. Lim

Hosts:

Dr. Y. Taniguchi	
Mr. M. Furuichi	High Purity Water
Mr. H. Motomura	Manager, Chromatography Division
Mr. T. Watanabe	Managing Director

BACKGROUND

Kurita is an engineering and chemical company the basic business of which relates to water. In 1991, its sales were about $700 million. Chemicals and water and wastewater treatment facilities each accounted for about 40 percent of revenues. Environmental control facilities (sewage, wave pools, water slides, etc.) contributed the remaining 20 percent. Water and wastewater treatment include high purity water for electronics and industrial wastewater, especially for auto, steel, foodstuffs, and so forth. Kurita also has a new biology department looking for microorganisms that will consume refractory waste materials.

Kurita has been interested in gray water recycling to provide a recycle system for sinks, showers, and other facilities, in hotels and apartments. Although the early systems were all membrane, Kurita says biological treatment is the current norm. Kurita also engineers process liquid chromatography under license.

Of interest in the separations area are Kurita's:

1. membrane moderated sewage treatment,
2. high purity water for semiconductor manufacturing, and
3. liquid chromatography.

Kurita has developed and promoted novel technology for handling high level human waste (night soil). It now produces equipment handling 40 percent of this material. This type of waste is not significant for the United States and will not be discussed further here.

Motomura, manager of the Chromatography Division, made a brief presentation of Kurita's activities in his division. Kurita has 70 percent market share in Japan for preparative high pressure liquid chromatography (HPLC) columns used in fine chemicals and pharmaceuticals. These systems are either engineered in-house or are sold under license from ELF. Columns are currently up to 600 mm diameter, and have pressure drop up to 70 bar. A column this size can process 15 kg of product in one 20-minute cycle. Stationary phase packings are 20-150 μm spheres (mostly around 50 μm), most commonly silica gel and chemically modified silica gel. Ion exchange materials are rarely used for HPLC. Modified dextrans were not mentioned, even though they are the cost standards for United States and European systems.

The JTEC team's impression was one of strong, reliable engineering.

High purity water is the area of Kurita's business that is of most interest to the team. Kurita claims to be number one in Japan, with approximately 40 percent market share, somewhat ahead of Japan Organo.

The team examined the flowsheet and then looked at individual operating elements of the process in Kurita's lab (see Fig. 3.1).

"Preblock" is the equivalent of a roughing filter, removing particles, colloids bacteria, and dissolved macromolecules. Kurita uses its proprietary UF spiral elements with the wide feed spacer. In doing so, the company claims that it can eliminate conventional coagulation, sedimentation and filtration steps. The CO_2 scrubber is a packed tower that uses filtered air as a stripping agent. Next the water is passed through two reverse osmosis units in series. These remove almost all dissolved species. O_2 is then lowered to 5 parts per billion (ppb) by stripping in a packed bed with 99.999 N_2. After a surge tank with N_2 blanket, O_2 is reduced further in a bed packed with ion exchange beads on which Pd has been coated, H_2 being the reductant. The O_2 level at the exit is < 1 ppb. Ion exchange is next, first cation then mixed bed, following a surge tank. Total organic carbon (TOC) is reduced via low pressure UV oxidation to < 2 ppb. The water is then passed through a special super purity mixed bed ion exchange resin and UF to produce specification-grade water.

Kurita claims that the solution for 16 megabit chips is essentially in hand. The company is now concerned about the 64 megabit generation of chips, expected in this decade. Kurita claims that new technologies need to be added to meet the demanding specs. When asked what the toughest-to-meet requirements were, the team was told TOC followed by heavy metals.

Kurita showed the team an internal document containing a graph of water system cost plotted against the log of chip intensity. For 1, 4, and 16 megabit memory chips, the cost was linear in log chip intensity, with the cost not rising as fast as the intensity -- that is, the cost was not doubling as the intensity doubled. After the 16 megabit generation, however, Kurita projects a slope break upwards. Considerable speculation is necessary at this point about which of a number of sketched-in curves will best describe the future systems. Our Kurita hosts stated that their customers are alarmed by the trend. The company also expressed confidence in its ability to develop technology that will bring these costs more into the historic trend.

Site 1:	**Ishinomaki Mill, Jujo Paper Co.**
Date Visited:	June 8, 1992
Site 2:	**Jujo Technology Center** **5-21-1 Oji, Kita-ku** **Tokyo 114, Japan**
Date Visited:	June 11, 1992
Report Author:	H. Muralidhara

ATTENDEES

JTEC:

Site 1:

H. Muralidhara
M. Wadsworth

Site 2:

C. J. King
H. Muralidhara
M. Wadsworth

Hosts:

Kiyoaki Iida	General Manager, Central Research Lab
Koichi Imamura	Senior Technical Engineer, Technology and Environment Dept.
Shigeru Ohyama	Deputy General Manager, Engineering Dept.
Yoshihiko Katagiri	Technical Engineer, Production Dept.
Sadaharu Takahashi	General Manager, Production Dept.

BACKGROUND

Japan is the second largest paper-producing country in the world; the United States is first. Japan consumes about 30 million cubic meters of wood annually. Approximately 70 percent of Japanese land is covered by forests; however, timber resources are not adequate to provide enough fiber. Japan's timber inventory ranks seventh in the world. Ishinomaki Mill is located in the northwest corner of Japan.

The mill's daily paper production is 2,500 tons per day (TPD), and the annual turnover is $830 million.

Ishinomaki is the largest publication-grade paper plant in the world. The plant is very modern. The visiting JTEC team could detect no odor coming from the plant in the nearby surroundings.

Wood chips are imported from Australia, Canada and the United States -- approximately 580,000 tons of bolt wood chips per year are imported into the country. Pulping is done using continuous digesters that provide significant energy savings. The technology used is Kamyr continuous digesters.

The energy source for Jujo falls into three categories:

Coal (Australia)	60 percent
Black liquor	35 percent
Oil	5 percent

Purchased electric energy cost in Japan is as high as 12 yen/kwhr. Hence, most of the energy is generated internally. The total power demand at Jujo is 150,000 kw. Jujo purchases 6,000 kw of electricity at the standard rate and 62,000 kw at a discounted rate. Trends for the purchased energy sources in Japan for the pulp and paper industry were reported during the team's visit at Jujo Central Research and are reported in Chapter 7.

Since Japan relies heavily on imported fuels, energy conservation is a key feature in Japanese industry. Japanese companies provide incentives to production workers to come up with good ideas in saving energy during processing -- for example, an invertor controlled motor or better sensing equipment that can save energy. Since the requirement in quality is increasing, the Japanese paper industry is buying newer equipment that is more energy efficient. Thus, Japan continuously adds capital to its industries, which helps Japanese companies run their operations more efficiently.

As far as bleaching is considered, Jujo is moving towards chlorine-free bleaching. Approximately 15 percent of the chlorine produced is used in the paper/pulp industry.

ENVIRONMENTAL FACILITIES

The company indicated that the dioxin problem in Japan is under control. No dioxin legislation or regulations are anticipated in the near future. Current regulations are based on informal mechanisms. By contrast, U.S. dioxin regulations are strict. Europe and Canada have the strictest dioxin controls in the world. However, the

Jujo Mill is moving towards chlorine-free bleaching to minimize the total organic halides (TOH) levels and thereby the dioxin problem. JEA performed a large-scale investigation and has concluded that the dioxin levels in the mill effluents are under control.

The environmental facilities at the mill are:

1. For effluent treatment (e.g., suspended solids, chemical oxygen demand, and color removal) -- five clarifiers, one of which is 106 meters in diameter, the largest of its kind in the world;

2. Two black liquor recovery boilers;

3. For sludge disposal, rotary kilns, screw presses and a sludge boiler;

4. Electrostatic precipitators (six for recovery boilers, two for pulverized coal boilers, and one for KP lime kilns);

5. Six scrubbers, five multicyclones and six sets of desulfurization equipment; and

6. For noise abatement, silencers and soundproofed walls.

CONCLUSIONS

Jujo has made no major breakthrough from a technological viewpoint. However, it must be emphasized that the company's process control and integration are outstanding. Although the company has capital invested heavily on the environmental side, it is still able to manufacture paper at a reasonable profit level.

One of Jujo's grievances was that the company buys all of its equipment from outside countries, such as Sweden, Finland, Germany, and the United States. The Japanese sometimes modify their design in order to operate very efficiently. It was indicated that companies such as Mitsubishi Heavy Industries, Kobayashi Iron Works and Aikawa Iron Works are attempting to develop paper/pulp equipment in Japan. They could be in the market.

APPENDIX D. SITE REPORTS - UNIVERSITIES

Site 1:	**Tohoku University** **Sendai 980, Japan**
Date Visited:	June 6, 1992
Site 2:	**Government Industrial Research Institute, Tohoku (GIRIT)** **4-2-1 Nigatake, Miyagino-Ku** **Sendai 088, Japan**
Date Visited:	June 6, 1992
Report Author:	M. Wadsworth

ATTENDEES

JTEC:

H. Muralidhara
M. Wadsworth

HOSTS:

Professor M. Tokuda	Tohoku University
Toshishige Suzuki	GIRI Tohoku

BACKGROUND

Tohoku University is well known for its work in metal separations. Major departments and institutes that the JTEC team visited were the Department of Metallurgy, Department of Chemical Engineering and the newly formed (April 10, 1992) Institute for Advanced Materials Processing (IAMP). The IAMP is under the direction of Professor Yoshio Waseda and is made up of four divisions:

1. Division of Materials Refining;
2. Division of Morphological Control;
3. Division of Materials Analysis; and,
4. The Research Center for New Metallurgical Resources[1] (under Professor Masanori Tokuda).

A presentation was made by Dr. (Professor) Hiroshi Sasaki of the Anticontamination Laboratory, a laboratory in the Division of Materials Refining. This laboratory, with a basic mission of preserving water and gas quality, is addressing specific problems such as:

1. Rapid separation of very low concentrations;
2. Rapid separation methods for removal of oil and emulsion from wastewater and sea water;
3. Electrochemical methods for metal refining; and,
4. In situ methods for the measurement of electrokinetic potentials of particles in suspensions.

Dr. (Professor) Fumio Saito made a second presentation. He is from the Mechanical Refining Laboratory and the Division of Materials Refining. In the metals separation and refining area, this laboratory is charged with:

1. Refining raw materials by using assorted mechanical forces, and
2. Extractive separation of metals from unutilized mineral resources by flotation.

Dr. (Associate Professor) Yoshiaki Umetsu -- in Dr. Tokuda's Research Center for New Metallurgical Resources -- made a third presentation. Dr. Umetsu reviewed hydrometallurgy technology newly applied in the treatment of concentrates and smelter intermediates. Dr. Tokuda showed us his laboratory facility with emphasis on their continuing work on supercritical liquid extraction processes.

Dr. Yonemato of the Department of Chemical Engineering reviewed current research on metals separations. Two projects reviewed were:

1. Bioextraction and separation of proteins, and
2. Recovery and separation of cobalt from manganese sea nodules.

These nodules are widely distributed on the ocean floor and are available about 2 km from the coast line at a depth of approximately 200 meters. Ammoniacal

[1] The Research Center for New Metallurgical Resources replaced the Research Institute for Mineral Dressing and Metallurgy.

leaching is employed for cobalt recovery. Cobalt is a critical material for high temperature alloys. These labs have standard equipment, but lack specialized instrumentation.

All JTEC team members met at the Government Industrial Research Institute for a presentation by Dr. Toshishige Suzuki, Chemical Product Development Division and Dr. Tomio Goto, Director of the Chemistry Department. The presentation centered on two areas of research:

1. New ion exchange (chelation) resins for specific ion removal, and
2. Development of impregnated porous resins for specific ion extraction and methodology for impregnation, stripping and regeneration.

TECHNICAL DETAILS AND OBSERVATIONS

Recent Developments in the Application of Hydrometallurgy to the Treatment of Ores, Concentrates and Smelter Intermediates

Metal separation processes in Japan must be designed as an the entire system in such a way that all effluents can be managed in an environmentally acceptable manner. Consequently special emphasis must be given to recycle streams to separate toxic materials, to prepare pure recycle water with contaminants (including colloidal suspensions) reduced, to develop value-added byproducts and non-reactive solid wastes. Also special emphasis is given to the recovery of less-common metals such as gallium and indium present in various ores and smelter streams that have value-added potentials because of specific industrial applications. Cobalt recovery from sea mining has been fairly successful.

GIRIT has developed ion-specific resins to increase specificity for recovery and purification of gallium and indium, as well as gold-chloride and precious metal chlorides from hydrometallurgical treatment of electronic scrap and residues.

Most metals come to Japan as concentrates of various grades and compositions; hydrometallurgy provides an opportunity to address complex problems for impurity and recovery of valuable components. In addition, our hosts emphasized that special consideration is being given to the skillful combination of hydrometallurgical and pyrometallurgical processes to improve economics and meet environmental needs.

Specific examples cited are:

1. Thiourea leaching of gold containing silicon ores has been carried to the pilot plant stage by Hishikari Mines in the Kyushu District.

2. A process for the treatment of residues from electrostatic precipitators in electric power generation has been commercialized.

3. A new plant for rare-earth recovery and purification was brought on-stream last year by Hanaoki Rare Earth Co.

4. Tests have been carried out for the treatment of flue dusts produced by iron blast furnaces.

5. Research is continuing on treatment of dust (containing high arsenic, etc.) from copper flash smelting operations.

In the area of metals recycling, processes have been developed for the treatment of spent catalysts for recovery and purification of metal components, for the treatment of electronic scrap for recovery of gold and other metals, and for the management of Cd in Ni-Cd batteries. In regard to the latter, Cd producers are currently proposing a new recycling network.

Bioextraction technology is currently employed by the Kosaka Works of Kosaka Smelting Co., Ltd. in the treatment of residues for the oxidation of Fe(II) to Fe(III).

New Developments in Solvent Extraction and Ion Exchange

This portion reviews only the work being carried out at GIRIT. The chemistry department has prepared two types of resin ion-exchange systems. The first consists of a series of resins for which a polymer matrix is bonded covalently with chelating functional groups. Because of the variable functional groups known for their chelating properties, a large variety of selective resins may be prepared by this bonding technique. Work has focused on the less-common metals for which ion exchange resins have been prepared. Several publications are available that describe these resins.

A second approach is related to the development of resins impregnated with extractants. Here commercial porous resins (Rohn and Haas Amberlite XAD-7 and XAD-4 were used) are impregnated with an organic extractant specific for certain anions or cations. The polymers are hydrophobic, thus keeping the extractant in the pore space with little loss. The technology is not new. What is new here is the method of stripping. In the place of conventional SI/IX stripping, the extractant plus its metals content are extracted using organics such as MIBK or acetone. The resin is then reimpregnated and reused. Very little attrition occurs and the resin may be used for many more cycles than is conventional. Recent research has focused on gold and platinum group chloride anions, gallium, indium, molybdenum, tungsten and scandium. Chromatographic separation of rare earths has been demonstrated using solvent impregnated resins.

Comminution

Work in the area of comminution has focused on ultrafine grinding. Several new grinding machines are commercially available. These are manufactured by Hosokawa Mikuron Co., Ltd. and Otsuka Tekkon Co., Ltd.

Comminution research is currently being carried out to simultaneously grind and chemically extract certain components. This is mainly a new initiative. Also work is continuing to improve grinding efficiency. One specific example of mechanochemical grinding is the method (recently described in the *Journal of Light Metals*) of removing aluminum-containing components from Bauxite.

Supercritical Extraction

Professor Tokuda, at a laboratory well equipped with several sizes of very high temperature/high pressure reactors, is studying several systems dealing with supercritical aqueous extraction.

Ultrafine Particle Separation

This research focuses on controlling charge characteristics of suspended colloid, such as hematite in iron recycle streams. In neutral solutions, isothetric points are determined and produced for hematite. The flocculation growth kinetics for various sizes have been quantified. Particle agglomerate size varies with initial crystallite size, so that after selected times particles many be separated by decantation. It has been shown, at the bench scale level, that the introduction of silica spheres may be controlled so the hematite colloidal particles attach to the quartz, and may then be separated from the aqueous suspending liquid.

CONCLUSION

These programs are focused on technology to prepare effluent streams of sufficient purity for recycling, marketing or discharge. The work on removal of colloids is novel but has been done only in the laboratory. The recycling of metals from electronic scrap and smelter streams is not likely to provide major new developments since most efforts are using demonstrated or previously commercialized technology. The value of supercritical extraction applied to metal extraction is academically important and may lead to commercial development in the future. Some value-added examples of metal purification from waste streams seem feasible in the Japanese economy. While industry has supplied some equipment, strong joint university-government research seems limited. The work at GIRIT on new resins and resin technology is innovative, but has not been commercialized.

Site: **Kyoto University**
Department of Chemical Engineering
Sankyo-ku
Kyoto 606, Japan

Date Visited: June 9, 1992

Report Author: C. J. King

ATTENDEES

JTEC:

G. Keller
C. J. King
H. Muralidhara

Hosts:

Professor Morio Okazaki
Professor Iori Hashimoto

BACKGROUND

The team visited three *koza*, headed by Professors Okazaki, K. Hashimoto and I. Hashimoto. Presentations were given by Professors Okazaki and I. Hashimoto, and by their associates (Tamon and Ohshima, respectively) and those of K. Hashimoto (Miura, Kawase).

TECHNICAL DETAILS

Metal-impregnated Carbon Adsorbents (Tamon)

Copper and palladium compounds are impregnated onto activated carbon. Through pi-bonding these elements interact preferentially with CO, and thus this approach presents possibilities for uptake of CO from gas streams. Loadings seemed to be unusually high (20 percent to 30 percent), giving problems of pore blockage and inefficient use of surface area and metal sites. Oxidation of copper from the cuprous state to the ineffective cupric state is also a problem.

Solvent Regeneration of Spent Adsorbents (Tamon)

Activated coconut-shell carbon is oxidized with aqueous HNO_3. Boehm titrations are used to distinguish among surface groups of different acidities. Up to 10 percent of the carbon is lost during treatment. Regeneration of adsorbed phenol with ethanol reveals that the oxidation process enhances regenerability, but lessens capacity. Neutralizing acidic carbons enhances the reversibility of adsorption of aniline, but not of phenol.

Adsorption of Uranium from Seawater (Tamon)

This research seeks to develop accelerated tests for determining equilibrium uptake of uranium by hydrated titania and amidoxime resins. (Ordinary equilibration takes as long as seven years.) The research has confirmed that uranium exists in seawater as uranyl carbonate $[UO_2(CO_3)_3]^{-4}$. Since all equilibria can be correlated with the concentration of this species, spiking of solutions with HCO_3^- leads to an effective accelerated testing method.

A conceptual design was presented in which a submersed folding-screen packed bed is used as an adsorber for uranium in seawater.

Gas Purification by Electron Attachment (Tamon)

A separator has been devised, working on the principle of the electron-capture detector. A gas stream is showered with electrons generated by a DC corona discharge, whereupon molecules bearing electronegative atoms become anions, which are transported to an anode and then separated. This method is felt to be most effective for removal of trace components, for example, ^{131}I. The presence of oxygen in the stream enhances the removal of sulfur compounds, presumably through a chain ionization reaction. This method of separation would be energy-intensive. The economics seem not to have been assessed.

Breakthrough Curves for Unknown, Multisolute Wastewaters (Okazaki)

Multisolute adsorption is modeled through a multicomponent Langmuir relationship, and a corresponding local-equilibrium theory is applied to predict breakthrough curves.

Molecular-sieve Carbons (Miura, Hayashi and Hashimoto)

A molecular-sieve carbon is prepared as follows. Phenol-formaldehyde resins or coal or coconut-shell carbons mixed with coal pitch are subjected to pyrolysis to form primary pores. Organic template substances, such as anthracene, are then added, and the resultant material is further pyrolyzed. Tracer adsorbing probes (gases with known molecular sizes) are used to assess the distribution of micropore sizes. With certain templates, that is, anthracene with phenol-formaldehyde resin, a sharp pore-size distribution in the range of 4Å is obtained. Such a sorbent can be applied to difficult separations. The pyrolyzed anthracene/phenol-formaldehyde adsorbent is capable of separating isobutylene from 1-butene, as well as propylene from propane.

Separation of Fructose and Glucose (Kawase)

This project carries out modeling of a conventional sort to describe simulated moving-bed absorbers. In earlier work (1983), a series of interspersed isomerization catalyst beds and adsorbent beds were used to gain a synergistic effect, wherein glucose is always being pushed by the chromatographic separation into the isomerization reaction zones.

Modeling Batch Distillation (I. Hashimoto)

This is a theoretical study to assess the effects of start-up policy and liquid hold-up on the efficiency of batch distillation. The possible benefits of adding a stripping section to batch stills is also being examined theoretically.

Synthesis of Sequences of Heterogeneous Separators (I. Hashimoto)

This theoretical synthesis problem is approached through the concept of allowing intermediate streams of only discrete, fixed composition. A combination of distillation and pervaporation units for ethanol-water separation has been used to test the method.

Estimation of Drying Rate Curves (M. Okazaki)

The regular regime theory of Schoeber and Thijssen is extended to allow for the difference between funicular and pendular water.

REFERENCES

Miura, K., J. Hayashi and K. Hashimoto. 1991. *Carbon, 29* 4/5: 653-660.

Miura, K., J. Hayashi and K. Hashimoto. 1991. *Proc. Intl. Conf. on Coal Science*. New Castle: 560-563.

Site: **Kyoto University**
Dept. of Biochemical Engineering
Sankyo-ku
Kyoto 606, Japan

Date Visited: June 9, 1992

Report Author: W. Eykamp

ATTENDEES

JTEC:

W. Eykamp
D. Roswell
M. Wadsworth
B. Williams

Hosts:

Dr. Shigeo Katoh
Professor Eizo Sada
Associate Professor Nasotaka
Dr. M. Tanigaki

BACKGROUND

Kyoto's engineering enrollment is about 1,000 undergraduates and 600 M.S. candidates each year. About 250 doctor of engineering degrees are granted per year. In chemical engineering, 50 undergraduates and 23 M.S. candidates are enrolled in each year. There are 14 doctor of engineering candidates in the department.

The first topic discussed was immunointeraction between antigens and antibodies and its application to separation.

Dr. Katoh described his research for the selection of affinity ligands for immunoaffinity chromatography. Using the findings that short synthetic peptides can generate reactive antibodies, the idea is to control the dependence of antibody affinity to environmental conditions by selecting peptides for their affinity for the target protein and their different response to changing environment. Clarifying the role of amino acids on the recognition site, they selected three peptides for investigation. One contained three histidine residues which, with pK 6, is unique among charged amino acids. A second peptide is free of charged amino acids, and has a low average hydrophilicity. A charged peptide with high average hydrophilicity is the third.

These peptides are attached to a common protein, such as BSA, to prepare anti-peptide antibodies which, when attached to column resin, produce liquids sensitive to pH and ion strength.

The second topic was homogeneous immunoassay utilizing liposomes, specifically how to detect proteins present at mg to $\mu g/\ell$. The steps were adsorption of an antigen, washing, and addition of an enzyme labeled antibody. A finding was that a fluorescent material that does not fluoresce at high concentrations could be incorporated into the cell membrane. Only when the cell wall was disrupted would the dye become dilute and thus fluorescent. This technique is being tested for use in sera for hepatitis, HIV, and others. Concentrations of antibody at 0.1 $\mu g/ml$ are enough.

Dr. Katoh's third topic was the reconstruction and immobilization of membrane-bound enzymes by use of liposomes. Membrane-bound enzymes are highly hydrophobic, and are not active in an aqueous environment. They may be solubilized with detergent, but their conformation changes. They lose their activity in purification. By reconstituting the enzyme into small unilamilar vesicles, activity of the membrane enzyme is retained for a month.

Associate Professor Masatoka Tanigaki described a membrane distillation project, starting with apparatus described in a patent by Gore. In the experiments he described, pore pressures in the Gortex dropped rapidly after a few days, causing the membrane to wet and fail.

A second interest is humidity control in buildings, looking for a lower energy alternative to humidity control than operating an air conditioner evaporator below the dew point. Current work relies on LiCl at 30 percent concentration, perhaps using a membrane conductor to indicate the absorption of water into the solution. Raising the temperature of the LiCl solution moderately drives off the absorbed water. Currently, they are thinking of using a larger inventory of LiCl and operating in unsteady state, perhaps using off-peak power to dehydrate the solution at night.

This study is part of a national program to make Japanese housing more energy efficient.

Site: **Kyoto University**
Department of Metallurgy and Department of Mineral Science and Technology
Sankyo-ku
Kyoto 606, Japan

Date Visited: June 10, 1992

Report Author: M. Wadsworth

ATTENDEES

JTEC:

H. McGee
M. Wadsworth
B. Williams

Hosts:

Dr. Yasuhiro Awakura	Associate Professor
Dr. Hiroshi Majima	Professor Emeritus, Department of Mineral Science and Technology
Dr. T. Wakamatsu	Professor of Mineral Processing
Dr. Yoshitaka Nakahiro	Associate Professor
Dr. Eishi Kusaka	Instructor
Maskazu Niinai	Research Associate

BACKGROUND

The engineering faculty at Kyoto University is associated with 23 departments covering a broad spectrum of engineering disciplines plus architecture, applied mathematics and physics, industrial chemistry, hydrocarbon chemistry, polymer chemistry and synthetic chemistry. In addition, there are two specialized divisions in molecular engineering and applied system science, and four laboratories. This engineering program is the largest in Japan and admits approximately 1,000 new students yearly.

The Department of Metallurgy and the Department of Mineral Science and Technology operate jointly. These departments have twelve chairs and cover four general areas of metals engineering. These are: 1) extractive metallurgy; 2) metallic materials engineering; 3) metallic materials science; and 4) metal forming and processing. Eighty new students are admitted yearly to the undergraduate program. Thirty-eight students are admitted yearly to the master's program, and the maximum annual enrollment in the doctor's programs is twelve.

The mineral processing program is one of six chairs in the Department of Mineral Science and Technology. The department admits forty new undergraduates and eighteen master's students yearly. Only a few doctoral students are admitted yearly.

Faculty of the Departments of Metallurgy and Mineral Science and Technology also staff an international program under the title of School of Metallurgy and Materials Science and described as the International Course for Graduate Research Studies (ICGRS). This course is aimed at graduate and postgraduate students of foreign countries who want to carry out advanced research in metallurgy while learning Japanese language and culture. Tuition and fees are waived for these students, and the monthly stipend (1992) is ¥180,500 ($1,388 at ¥130/$).

TECHNICAL DETAILS

Drs. Majima and Awakura have achieved worldwide recognition in metals separation for their basic research in leaching models and mechanisms, thermodynamic properties of electrolytes used in metals extraction, solvent extraction and metals reduction. Dr. Majima has completed pioneering work in elucidating electrochemical properties of minerals and metals related to various processes of extraction. These researchers are noted for their innovative techniques and for the high quality of their research, which has been published extensively in U.S. and Japanese literature.

Dr. Awakura is planning new directions for their research efforts. An innovative example is continuous solvent extraction using a potential gradient to disperse the loaded aqueous phase in the organic extractant using a solid electrode and a mesh electrode to establish the potential gradient. The mesh electrode serves as a diaphragm through which loaded organic diffuses. Stripping is carried out on the opposite side of the mesh electrode. Descending aqueous phase separates in a quiescent zone in the bottom of the cell producing raffinate on one side of the cell and aqueous strip solution on the other. Current research focuses on nickel separation.

A second example is research in electroless plating. The approach is novel in that metal hydroxides, for example, nickel or copper hydroxide, are adjusted to pH values where hydroxide is near its zpc (zero-point of charge). The hydroxide then adsorbs on the surface of the object to be plated. A reductant such as KBH_4 is added, producing reduced metal layers on the surface. This technique may be applied to the formation of some composites. An example is the plating of graphite to improve its conductivity when used in electrical contacts.

Drs. Majima and Awakura recently completed interesting new studies on copper separation by cementation. This work, published in June 1992, explains the often observed shift in reduction kinetics during cementation.

Dr. T. Wakamatsu reviewed research in mineral processing. Four major areas of research are: 1) use of grinding aids to reduce the energy of grinding; 2) separation of graphite from iron-plant flue dusts by flotation; 3) recovery of synthetic diamond by flotation; and 4) liquid/liquid flotation.

With regard to graduate research, facilities in almost all graduate schools appear inadequate. Many graduate students carry out their research on company sites. The research is directed by faculty members and coordinated with each participating company.

CONCLUSIONS

Faculty members at Kyoto University's Department of Metallurgy will continue in their tradition of carrying out world-class research in metal extraction. The research is fundamental in character. Students from the program enter industry with a strong academic background. Industry is cooperative in providing research facilities for some of the graduate students. Physical plant facilities are in need of modernization. Equipment is good but conditions are crowded.

Site: **Osaka University**
1-1 Machikaneyama-cho
Toyonaka 560
Osaka, Japan

Date Visited: June 9, 1992

Report Authors: W. Eykamp
M. Wadsworth

ATTENDEES

JTEC:

W. Eykamp
H. McGee
H. Muralidhara
D. Roswell
M. Wadsworth

Hosts:

Professor I. Komasawa
Professor Setsuji Tone
Associate Professor M. Taya
Associate Professor Yushi Hirata
Dr. T. Masawaki
Associate Professor T. Nitta

DISCUSSION (Eykamp)

Professor Komasawa gave a general introduction of the separation process group. Then Dr. Taya briefly introduced the Reaction System Engineering Laboratory, which is interested in heterogeneous chemical reactions, multiphase flow reactor design, studies on biochemical reactions and bioreactor systems with enzymes, microorganisms and plant cells, and studies on membrane separations systems based on the physical and chemical interactions between membranes and solutes.

Dr. Hirata gave a review of the project on separation of rare earth elements by electrophoresis.

Dr. T. Nitta gave an overview of the fundamentals of equilibrium separation processes. Particularly they study mass transfer rates in separation processes, including supercritical fluids, adsorption chromatography, and liquid extraction in an electrical field.

The group then divided into three subgroups. This author went with the membrane subgroup along with David Roswell, and Drs. Tone, Taya and Masawaki.

Dr. Taya reviewed his work on extractive butanol fermentation. In order to overcome the problem of end-product inhibition while maintaining a low energy separation, his group surveyed a number of materials to find one that is immiscible, is nontoxic to the microorganism of interest, and has a high partition coefficient. For the extractive fermentation of butanol, oleyl alcohol was the choice; the partition in the concentration range of interest was linear (mass concentration) with a slope of 3.7. The oleyl alcohol was withdrawn from the reactor and stripped of butanol in a hollow fiber pervaporation device. Butanol concentration was about 2.5 kg/m^3 in the aqueous phase, 10 kg/m^3 in the oleyl alcohol phase, and 500 kg/m^3 in the pervaporation condensate.

Dr. Masawaki described his work on chiral resolution by ultrafiltration. The technique was to prepare an enantio-selective membrane by condensing L-phenylalanine onto the polysulfone UF membrane with glutaraldehyde. The membrane passed D-phenylalamine in preference to the L isomer. Because of the observation that self-associates between L and L isomers are more stable than those between L and D isomers, the high concentration of L isomer bound in membranes' pores retarded the passage of the L isomer through the membrane. At very low flux in a diffusion experiment α of 4 was observed, but at normal UF fluxes, the α approached 1.

METALS SEPARATION (Wadsworth)

New research in metals separations focuses on rare earth extraction, recovery of metal values from waste streams, and novel technology for electrochemical and photochemical reduction of rare earth and electrophoretic separation of rare earths. Gallium and many other metals in coal fly ash have been recovered in the laboratory through leaching and solvent extraction. Economic feasibility was not demonstrated. The selective reduction of europium (Eu^{3+} Eu^{2+}) electrochemically and photochemically has been shown to occur in laboratory tests; Eu^{2+} is removed by precipitating $EuSO_4$. Small-scale electrophoretic separation of rare earths was carried out producing separate streams with high selectivity. Economic evaluation and studies on the possibilities for commercialization have not been completed. There was no evidence of university-industry joint research in these areas; therefore, there is no way to know what has been accomplished in private laboratories.

Site: **University of Tokyo**
Department of Chemical Engineering
7-3-1 Hongo, Bunkyo-ku
Tokyo 113, Japan

Date Visited: June 11, 1992

Report Author: C. J. King

ATTENDEES

JTEC:

C. J. King
H. Muralidhara
M. Wadsworth

Hosts:

Professor Shoji Kimura (also President of the Japan Membrane Society)

BACKGROUND

Professor Kimura heads one of six *koza* in chemical engineering, and one of twenty-five *koza* in the formerly combined fields of industrial chemistry, chemical engineering, synthetic chemistry, and reaction chemistry. The Kimura *koza* includes one associate professor (Shin-Ichi Nakao), one assistant professor at the postdoctoral level, one technician, two to three Ph.D. students, six M.S. students, and five to seven B.S. students. (A B.S. thesis is required.) The building facilities occupied by Professor Kimura are somewhat inferior to those at most U.S. universities, but are superior to those that the panel encountered at Kyoto, Tohoku, Osaka and Yokohama universities. There are adequate fume hoods. Supporting instrumentation for the applied chemistry *kozas* are impressive. Financial support (exclusive of salaries) is derived from about ¥2 million from the Ministry of Education, ¥8 million from industry, and ¥2.5 million from the Japanese equivalent of the U.S. National Science Foundation.

TECHNICAL OBSERVATIONS

Professor Kimura's group deals with many topics, all related to membrane separations. These fall in the general categories of reverse osmosis, ultrafiltration, charged RO and UF membranes, microfiltration, pervaporation, and gas separations.

It is surprising that so many topics would be undertaken by a group of this size. Among the specific subjects of investigation are:

1. Identifying membrane properties that optimize membrane area and pumping power for separations of organics and water by reverse osmosis.

2. Adapting transport analyses to cover high concentration ranges in reverse osmosis.

3. Development of a poly(tetramethylsilylpropylene) membrane that passes organic substances (e.g., ethanol) preferentially over water.

4. Development of sulfonated polysulfone membranes that will separate charged and uncharged species.

5. Research on layered cation- and anion-exchange membranes that are selective for monovalent species over polyvalent species. (This research would appear to support the Tokuyama Soda process based upon such membranes for recovery of NaCl from seawater.)

6. Development and identification of microporous membranes having narrow pore-size distributions, as measured by the conventional technique of freezing and melting within a differential scanning calorimeter (DSC).

7. Comparison of rates of vapor permeation with rates of pervaporation, under the same fugacity-difference driving forces.

8. Grafting of polymers onto microporous membranes to fill holes and thereby alter permeability and selectivity.

9. Removal of carbon dioxide from stack gases (a MITI project).

10. Adjustment of membrane pore size by deposition of silica resulting from the reaction of ozone and silicon vapor diffusing into pores from opposite sides of a membrane.

CONCLUSIONS

Professor Kimura is working on a variety of topics in the area of membranes. He covers a broad spectrum of activities ranging from microfiltration to pervaporation membranes. Rather than striking off in quite new directions, the work appears to be more in the line of direct extensions of concepts already in the literature.

Laboratory facilities at this location are better than those at some of the other Japanese universities visited.

Site: **Institute of Industrial Science**
University of Tokyo
7-22-1, Roppongi, Minato-ku
Tokyo 106, Japan

Date Visited: June 11, 1992

Report Author: M. Wadsworth

ATTENDEES

JTEC:

D. Roswell
M. Wadsworth
B. Williams

Hosts:

Dr. Noboru Masuko — Professor of Metallurgical Chemistry

BACKGROUND

The University of Tokyo was established in 1877. Presently the university consists of 10 faculties, 12 institutes and 11 graduate schools. Of the 12 institutes, the Institute of Industrial Science is the largest. The institute is not structured on the *koza* system. Each faculty member functions separately. In addition to carrying out individual research, these faculty members also contribute to the graduate program by directing graduate student research and teaching graduate course work. The Institute of Industrial Science is made up of 109 laboratories. Each is supervised by a professor, associate professor or lecturer. These individuals separately determine the research undertaken in the laboratory. The 109 laboratories are grouped into 5 departments and 3 research centers. The institute receives the major portion of its budget from the Ministry of Education, Science and Culture, and a part from industry. The institute operates on a fixed base budget for research plus additional funding based on written proposals. Special institutional proposals are submitted to the ministry for capital equipment. A portion of the total budget is reserved for distribution to selected junior academic staff members. Based on requests from industry, the institute carries out cooperative research with these companies. Experienced personnel from industry are permitted to use the laboratory in joint research efforts. Support from industry therefore funds the ongoing research and additional funds support endowed chairs supervised by visiting professors or associate professors from outside. In addition to graduate education and research, the institute is involved in the continuing education of junior engineers and scientists. Statistics from 1989 indicate that the institute carried out joint research with industry for 10 projects with a total budget of approximately ¥229 million. In addition it carried out contract research with industry, with 18 contracts totalling approximately ¥67 million. There were 431 donations and grants from private companies as a result of promotion, with total funding estimated at ¥426 million ($3.277 million at ¥130/$). In 1989 there were 56 visiting research personnel from industry. Research in metals separation is carried out by a few faculty members within the Department of Industrial Chemistry and Metallurgy. Of the 24 faculty members in this department, about 2 carry out research in metals separation technology.

Recent research in metals separation technology includes such areas as studies on high performance liquid chromatography, development of optical fiber sensors with functional membranes, and studies on ion exchange resin and membranes. A recent project on environmental and chemical engineering covered rates of adsorption and water quality management in the open environment. In the area of organic reaction, chemistry research has been carried out on the development of highly selective and efficient transport systems and ligand design of transition metal complexes. In environmental chemical analysis, research has been carried out on the design of membrane transport systems. In the area of particle technology, research has been carried out on the production and application of ultrafine particles, electrostatic formation of ceramic membranes, and particle size analysis.

TECHNICAL DETAILS

Dr. Masuko provided a detailed review of metals separation technology in Japan relevant to the JTEC panel's interests. In the areas on electrowinning, Nippon Mining Company is electrowinning both indium and thallium. Technology has been developed for the removal of chloride ions from zinc sulfate solutions in roast-leach-electrowinning circuits. This is achieved by adding copper to the circuit which, in the presence of chloride ions, precipitates solid cuprous chloride that is removed from solution. This appears to be an innovative way to remove chloride ions from zinc sulfate electrolyte. In the fall of 1992, Sumitomo Metals and Mining Company announced a new technology related to the treatment of matte anodes of composition Ni_3S_2 (from International Nickel Company). The technology involves the treatment of cuprous chloride for the recovery of HCl used in the process. This research is an extension of ongoing chlorine research that has been used recently for successful treatment of ferrous sulfide concentrates containing nickel. The chlorine reaction produces ferrous chloride plus elemental sulfur.

In another area Asahi Chemical Industries Company has been carrying out research for many years on stable isotope separation of ^{238}U and ^{235}U. This is done by rapid solvent extraction exchange in which approximately 5 million steps occur with a time constant of approximately 0.1 seconds per stage. Over the last 20 years, ¥30 billion has been expended in this research. In the area of roast-leach-electrowin (RLE) technology, Japan has achieved a very high state of specialization. The most recent advancements have to do with energy conservation. This is achieved in two ways. The plant is automated to work on very high current density during off peak hours and low current density during high peak hours. The low current density must not fall below 50 amps per m^2 or zinc metal will be redissolved in the system. During the high current density operation the mean current density is 600 amps per m^2, with an average current density of 450 amps per m^2. This has now been adopted generally as part of the RLE technology. A second method for conserving energy has been a major change in anode spacing from approximately 3 centimeters to 2 centimeters. This work has been spearheaded by Mitsubishi Metals Company. The problems that normally would be realized by shorting the distance would have to do with warpage and formation of dendrites. This is managed by an automated system in which the anodes are loaded into cassettes and handled by an automated mechanical system.

In the area of zinc secondary recovery, zinc dross is recycled for hydrometallurgical recovery of zinc. A special problem that must be addressed has to do with the presence of chloride ions. Dr. Masuko feels that technology to remove small concentrations of chloride ions from other effluent streams is very important. This research will become a major part of his activity in the future, when he develops a program to reduce contamination from the level of 1,000 parts per million to below 100 parts per million.

CONCLUSIONS

The Institute of Industrial Science is conducting limited research in the area of metals extraction. The Institute, however, has good ties with industry and seems to share research efforts on a project by project basis. While the physical plant facilities leave much to be desired, equipment seems to be excellent and focused on important problems related to industrial separation of metals. The emphasis on controlling chloride contamination in sulfate solution chemistry is an important problem in Japan that is being focused on by the Department of Metallurgy. The institute fulfills an important role in graduate education and in basic and industrial-related research.

Site: **Yokohama National University**
Hodogaya-ku
Yokohama 240, Japan
and
Tokyo Institute of Technology
Meguro-ku
Tokyo 152, Japan

Date Visited: June 15, 1992

Report Author: E. Cussler

ATTENDEES

JTEC:

E. Cussler

Hosts:

Professor Harohiko Ohya	Yokohama National University
Professor Jiro Komiyama	Tokyo Institute of Technology
Professor Akihiko Tanioka	Tokyo Institute of Technology

BACKGROUND

After the rest of the JTEC team had departed, this author visited two more universities. The former was my host for the International Symposium of the Society of Fiber Science and Technology (Japan). The latter was suggested by Gene Lim as a leading academic center of Japanese membrane technology.

Within the universities, the research seems reasonable, though rarely outstanding. It is comparable with that in U.S. universities, and is more frequently responsible for good scholarship than commercially important discoveries. Three specific topics, all dealing with membranes, seemed strong -- those of Professor Harohiko Ohya at Yokohama, and those of Professors Jiro Komiyama and Akihiko Tanioka at Tokyo Institute of Technology.

Professor Ohya's work centers on gas separation with ceramic membranes. His original targets of hydrogen and CO_2/CH_4 gave the usual low Knudsen selectivities obtained by other groups. These are only academically interesting. He now is focused on high temperature ammonia separation and membrane reaction. On ammonia separation, he aims at a hydrogen-permeable membrane rather than an ammonia-permeable membrane. On the membrane reactor, he is mainly interested in a hydrogen permeable membrane for high-temperature water splitting. This membrane actually will split the HBr part of a more complex chemical scheme (Fig. Yoko.1), and so faces significant corrosion problems. Professor Ohya has sound designs to facilitate module assembly. He does not seem to have thought out the membrane reactor ideas as completely as has, for example, Bend Research.

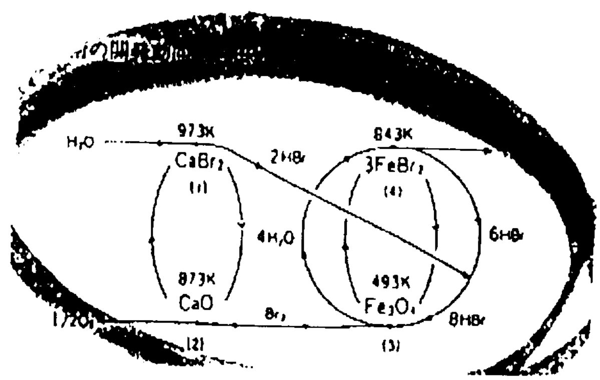


Figure Yoko.1. Water Splitting. The scheme shown requires a lower temperature than the splitting of pure water alone.

Professor Ohya has a broad perspective on membrane research in Japan. He expressed several opinions of interest. First, Ube's polyamide hollow fibers, developed for conventional separations like H_2/CH_4, may find their greatest application in air drying. Second, Aqua Renaissance, sponsored by MITI, divided its resources among too many sites. Third, water ozonation will replace chlorination because of rules of the Ministry of Health. This implies developing UF membranes to remove the precursors of halogenated organics, and will be carried out by industry, with Kurita in a lead role. The targets include removing 10μm particles from 40 x 10^6 m^3/day of water by use of membranes with a 10 psi pressure drop and a 98 percent yield (i.e., 98 percent of the feed will be permeate). Such performance implies using flocculent aids.

The work at Tokyo Institute of Technology was more specific. Professor Komiyama has doped water-swollen polyvinylalcohol membranes with salts like lithium chloride to get O_2/N_2 selectivities as high as twenty. While this surprising result may be an artifact, a search yielded no evidence of such in the actual data. Professor Tanioka has studied amino acid and other amphoteric solute transport across ionic membranes. Most results seem consistent with careful theory.

Site:	**Industrial Products Research Institute (IPRI)[1]** **MITI/AIST** **1-1-4 Higashi, Tsukuba City** **Ibaraki-ken 305, Japan**
Date:	June 12, 1992
Report Author:	C. J. King

ATTENDEES

JTEC:

C. J. King
H. Muralidhara
M. Wadsworth

Hosts:

Dr. Kazue Nishihara	Director General
Dr. Sumio Yamada	Organizer
Dr. Kazuhisa Hiratani	
Dr. N. Minoura	

BACKGROUND

The Industrial Products Research Institute (IPRI) is one of sixteen laboratories reporting to MITI. The laboratory has about 100 researchers and 23 administrators, with an annual budget of about ¥2 billion. Research is carried out through independent principal investigators. The JTEC team visited primarily the Materials Science Department, which has nine research terms and an annual budget of ¥50 million, exclusive of salaries. Researchers in this group are primarily synthetic organic chemists.

[1] As of January 1, 1993, IPRI and several other MITI institutes have been combined into the new National Institute of Materials and Chemical Research.

TECHNICAL DETAILS

Supported Liquid Membranes (K. Hiratani)

Novel ionophores are being synthesized as agents capable of accomplishing separations through reversible complexation carried out in supported liquid membranes. The compounds are ethers with noncyclic polyethers, picked through knowledge of the complexation properties of natural ionophores. In one interesting example, lithium is transmitted selectively from a mixture of alkali (Li, K, Na, etc.) salts by one agent, while potassium is selectively removed from the same mixture by another regent. Kinetics are sometimes slow.

In another application, a surprisingly high selectivity of 1.025 is obtained between ^6Li and ^7Li. This is thought to reflect differences in vibration energy levels. In still another application with practical importance, covered under patents, Cu^{2+} is selectively recovered from a mixture of Fe, Ni, Co, etc.

Gas Separation Membranes

High-pressure sorption experiments measure uptake capacity (gravimetrically) and swelling (change in dimensions). Permeation measurements are made by the standard (Barrer) combined unsteady-state/steady-state method at pressures up to 150 atmospheres. This research serves to characterize polymers and membranes.

Biomimetic Stimulus-Response Membranes (N. Minoura)

Stimuli are applied to synthetic polypeptide membranes to alter their permeability and selectivity properties. The stimuli cause the membrane to change between a consolidated, folded-molecule structure and a more open structure. Stimuli are applied at varying frequencies. In one implementation calcium ions are added to and subtracted from membranes to alter the rate of transport of Vitamin B-12. In another, pH is the swing variable, altering the separation factor between glucose and various chloride salts. Silk protein membranes have also been used in this research.

Novel Polymers and Pervaporation (S. Yamada)

In this work, currently inactive, a variety of novel polymers are synthesized, converted to membrane form, tested for properties, and, where appropriate, used for studies of pervaporation of ethanol-water mixtures. Selectivity has been achieved for either ethanol or water, depending on the membrane.

Site: **National Chemical Lab for Industry (NCLI)[2]**
MITI/AIST
Tsukuba, Ibaraki 305, Japan

Date Visited: June 12, 1992

Report Author: W. Eykamp

ATTENDEES

JTEC:

E. Cussler
W. Eykamp
G. Keller
D. Roswell

Hosts:

Dr. Chiyoshi Kamizawa
Dr. Toshio Shino

BACKGROUND

The National Chemical Lab for Industry (NCLI) has an expansive charter, so it is more instructional to look at actual projects. The team examined seven separator projects and was given a list of membrane projects, many of which were complete. The following is a description of the projects visited by the team:

Supported Liquid Membrane for Optical Resolution of Amino Acids (Dr. Shino)

This study uses Cram's crown ether as a reagent to selectively permeate one optical isomer. Their separation factor for a cell agrees with Cram's value of 20, but the productivity is very low.

Nonaqueous UF and RO by Phase Inversion Polyethersulfone, Polyvinylidene Fluoride and Polyimide Membranes

A variety of membranes have been prepared and tested for polyethylene glycol rejection using methanol and toluene as solvents. A 95 percent rejection of PEG 400

---

[2] As of January 1, 1993, NCLI and several other MITI laboratories have been combined into the new National Institute of Materials and Chemical Research.

is obtained. They test at 40 atmospheres and 25°C. Projected applications are in separations for the fats and oils industry.

This project also uses chemical vapor deposition to make very thin polyimide membranes. These membranes are useful for ethanol - H_2O. They give separation factors of 900 at a flux of 1 kg/m^2 hr.

At 900°C, these membranes carbonize giving a membrane with H_2/N_2 selectivity of 300, albeit with very low flux.

Rotating Disk UF Membrane (Dr. Masuda)

Counter-rotating overlapping disk membranes were tested at the Aqua-Renaissance site in Chigasaki. The disks are 50 cm diameter and have membrane on the outside. They are made by Hitachi. The goal was to achieve very low energy cost.

At 100 rpm tip speed is 2 cm/sec. On a stream having 10,000 ppm BOD, the energy requirement was 0.8 kwh/m^3. Flux was quoted at 1.5 m/day (or, in other units, 17.4 μm/sec or 62 ℓ m^{-2}h^{-1}). Hitachi Plant Engineering Division is the maker. The team learned that the department has only one to two people.

Chemical Vapor Deposition (Dr. Yanagishita)

The team was shown an impressive high vacuum chamber in which small samples could be coated with low volatility monomers in 10 min to 30 min. Monomers could be applied sequentially or simultaneously through the use of a shutter system. Plans are underway to convert the membrane holder to a hot stage so that membrane forming reactions could be completed in situ. The pressure limit is set by the mean free path, requiring 10^{-6} torr.

Chemical Reaction Membrane (Dr. Itoh)

The model being studied is $C_6H_{12} \rightarrow C_6H_6 + 3H_2$. Since this reaction is reversible, removing the H_2 pushes it to the right. To do this, Dr. Itoh uses a palladium membrane. As is known, pure Pd does not last long in the presence of H_2, so he has tried a variety of alloys and is currently using 23 percent Ag 77 percent Pd. His film thickness is 0.2 mm.

Permeation rates for Pd are unusual due to the chemical nature of H_2 transport. The driving force factor is $(p\ H_2)^{1/2}$ high - $(p\ H_2)^{1/2}$ low.

The use of palladium-alloy membranes for selective hydrogen permeation was commercialized in the United States in the late 1950s. The general concept is the subject of many technical articles. Dr. Itoh's work continues this tradition.

In spite of a tremendous research effort, the team knows of no commercial instances of using these metal membranes for dehydrogenation reactions elsewhere. The membranes are susceptible to poisoning and their fragility accentuates their inherent cost. Furthermore, competing processes are quite advanced and are reasonably economical. Recent findings of other cheaper and more rugged membranes with comparable properties represent formidable competition for the palladium-alloy approach.

Supercritical Fluid Separation (Dr. Sako)

This program is working with the use of supercritical fluids for the separation and purification of bicyclics from tricyclics. It uses CO_2. Of somewhat greater interest to the group was the reaction of hemicellulose to produce furfural in a supercritical chamber -- an analog of reactive distillation. The team was told that in the conventional reactor, much of the furfural disappears into side reactions. The scheme is to run in a chamber containing supercritical CO_2, topped by a column in which a temperature gradient is maintained such that the pot is at 421°K and the condenser is at 343°K. These are conditions where water drops out on the way up the column and furfural does not. SRI is investigating the economics.

Heat Integrated Distillation (Dr. Nakaiwa)

By running rectifying and stripping columns at different pressures and by using superior heat transfer technology to move heat around the column it is possible to reduce the energy of distillation.

The impetus for this work is apparently recent success in improving the efficiency of compressors in heat-pump cycles. This technology is used to compress the vapor to the rectifying section so that the temperature profile in this section will be higher than that in the stripping section. This permits heat to flow from the rectifying section, where heat is normally given up, to the stripping section, where heat is consumed. Dr. R. S. H. Mah at Northwestern University has published on the mathematics of this process. The technological and economic challenge for this process is to create an economical column geometry that will facilitate heat transfer from one section of the column to another while maintaining excellent mass transfer between vapor and liquid within each section.

Several U.S. companies have studied heat-integration distillation experimentally and conceptually, but have not yet commercialized it. In the higher energy cost economy of Japan, there is greater incentive for commercialization, but capital costs must still be a major concern.

Site: **National Institute for Resources and Environment (NIRE)**
MITI/AIST
Tsukuba, Ibaraki 305, Japan

Date Visited: June 12, 1992

Report Author: M. Wadsworth

ATTENDEES

JTEC:

C. J. King
G. Lim
H. McGee
H. Muralidhara
M. Wadsworth

Hosts:

Dr. Osayuki Yokoyama	Director General
Dr. Tetsuo Nakayama	Deputy Director General
Dr. Michio Kuriyagawa	Director, Research Planning Office

BACKGROUND

The National Institute for Resources and Environment (NIRE) is one of the core organizations of MITI's Agency of Industrial Science and Technology (AIST). The mission of NIRE is to promote research in the development and use of natural resources and energy. This is to be done in the context of assessing and controlling the global impact of this technology. Emphasis is placed on the generation of CO_2, understanding its life cycle, and correlating resource and energy development to minimize the impact on human life. The emission of halocarbons and novel techniques of adsorption and desorption technology to control halocarbons are part of the research. Other activities include acid rain observation and modelling, biological treatment of hazardous chemicals, and treatment and recovery of biological waste with supercritical fluids. The divisions within NIRE are the: 1) Global Warming Control Department; 2) Photo-Energy Application Division; 3) Combustion Engineering Division; 4) Hydrospheric Environmental Protection Department; 5) Environmental Assessment Department; 6) Energy Resources

Department; 7) Materials Processing Department; 8) Mining and Geotechnology Department; and, 9) the Safety Engineering Department.

Global warming research is carried out to address and verify material balances and to develop global models to assess the cyclic behavior of pollutants such as CO_2 and CFCs (chlorofluorocarbons). These models are to consider chemical and biological processes that influence the cyclic patterns of these pollutants. Specific areas of research are: 1) monitoring and analysis by remote sensing; 2) the carbon cycle in the Northwest Pacific; 3) fixation by catalytic hydrogenation; 4) NO_x control by fluidized bed combustion; and 5) recovery of CO_2 on various adsorbents.

Energy research at NIRE is focused on liquefaction and gasification of coal, biomass energy and geothermal energy. Research is also carried out on marine resources with emphasis on cobalt recovery from manganese crusts and nodules and base metals from polysulfide marine deposits.

TECHNOLOGICAL DETAILS

The team was shown many laboratories, all of which were very well equipped, spacious and very clean. Three areas of research were emphasized. The first of these was research on processing coal liquids from Australian coal. This is an extension of the Nedol process. In the process, separation of phenolic compounds and an upgraded oil is achieved. The second area of research is on the use of supercritical liquids to recover biological wastes. The equipment is the Kobelco high pressure press and monitoring equipment. The equipment was demonstrated to the JTEC team, but specific successes were not presented. Thirdly, research in ecological chemistry and microbiology was reviewed. NIRE has developed a membrane bioreactor for wastewater treatment. Research addresses hazardous chemicals from the sea, isolation of potentially useful bacteria and the development of new strains. Few details or successes were presented.

CONCLUSION

The NIRE research center is well equipped, clean and spacious. It contrasts with most university settings in terms of physical plant facilities. The treatment of coal liquids seems to be an area of emphasis but few details were presented on advancements and new developments that may be near commercialization in the area of separations. The research appears long range in scope. Few specific developments in marine resource recovery were provided, but it appears research here, as well as on coal liquids, is mainly of interest to Japan.

Site: **Research Institute for Polymers and Textiles[3]**
MITI/AIST
1-1-4 Higashi, Tsukuba City
Ibaraki-ken 305, Japan

Date Visited: June 12, 1992

Report Authors: G. Keller
E. Cussler

ATTENDEES

JTEC:

E. Cussler
W. Eykamp
G. Keller
D. Roswell

Hosts:

Dr. Takashi Tamaki	Senior Officer for Research Planning
Dr. Kensaku Mizoguchi	Chief Researcher, Process Engineering Laboratory

BACKGROUND

The Research Institute for Polymers and Textiles (RIPT) is one of a cluster of government laboratories in the Tsukuba area. RIPT was born in 1918 as The Silk Laboratory. In 1937 it was reorganized as the Textile Research Institute. Since then it has undergone numerous reorganizations and added several new departments and laboratories. In 1988 RIPT was reorganized into four major departments: polymer chemistry, bioengineering, material physics, and material design and engineering. The research and development carried on has six missions: 1) development of new technologies for the synthesis and structuring technologies of polymeric materials; 2) creation of molecular functional materials; 3) creation of biofunctional materials; 4) creation of high-performance composite materials; 5) upgrading system and process technologies; and 6) upgrading technologies of measurement, analysis and evaluation of materials.

---

[3] As of January 1, 1993, the Research Institute for Polymers and Textiles (RIPT) and several other MITI laboratories have been combined into the new National Institute of Materials and Chemical Research.

RIPT receives all of its funds from the government and is not permitted to receive money from industry. This organization has only a small fraction of its budget devoted to separations, and a large fraction of that amount is associated with membranes.

TECHNICAL DETAILS AND OBSERVATIONS

Pervaporation is a major focus of the membrane studies at RIPT. Most of this work is on a rather fundamental level in support of membrane technology in Japanese companies. Studies are underway on elucidation of the mechanism of pervaporation and on advanced methods for membrane fabrication. Plasma treatment is a primary treatment method for polymerizing monomers on the surface of a porous substrate. A national project is underway using plasma graft polymerization with a hydrophilic monomer. The substrate is polypropylene (CELGARD). Polymerization of fluorocarbon monomers such as perfluoropropylene onto polysulfone is also being investigated. This membrane is organophilic and will selectively permeate ethanol compared to water, for example.

An innovative project underway is the study of the use of pervaporation as a means of removing trace amounts of organics from groundwater. Membrane modules are buried in the ground in the water flume. Water is free to percolate into the shells of the permeators. Air is pumped underground and blown through the fibers, and the organics permeate selectively into the air stream. An activated-carbon adsorption bed can then be used to remove the organics from the air before it is released to the atmosphere. A diagram of the process is given in Figure RIPT.1. In spite of the intriguing nature of this technology, no commercial interest has yet been shown in Japan.

Dr. Mizoguchi focused his technical comments on pervaporation. He downplayed his work to give an overview of pervaporation work in Japan. As in Europe, the Japanese are thinking first of ethanol-water separations. As elsewhere, they are extending this to isopropyl alcohol-water and to trace organics in water. Specific systems include:

1. Plasma-treated hydrophilic membranes for separating traces of water from ethanol. RIPT researchers treat microporous polypropylene sheet with plasma to generate free radicals on the surface. They then coat with acrylic acid or HEMA (a polyacrylic gel) to get a nonporous 10 μm water-permeable skin.

2. Plasma-treated hydrophobic membranes for separating traces of ethanol from water. RIPT plasma-polymerizes fluorocarbons on microporous polysulfone to make a flexible nonporous 1 μm skin. These membranes have an alcohol-water selectivity of 10 and twice the flux of the GFT films.

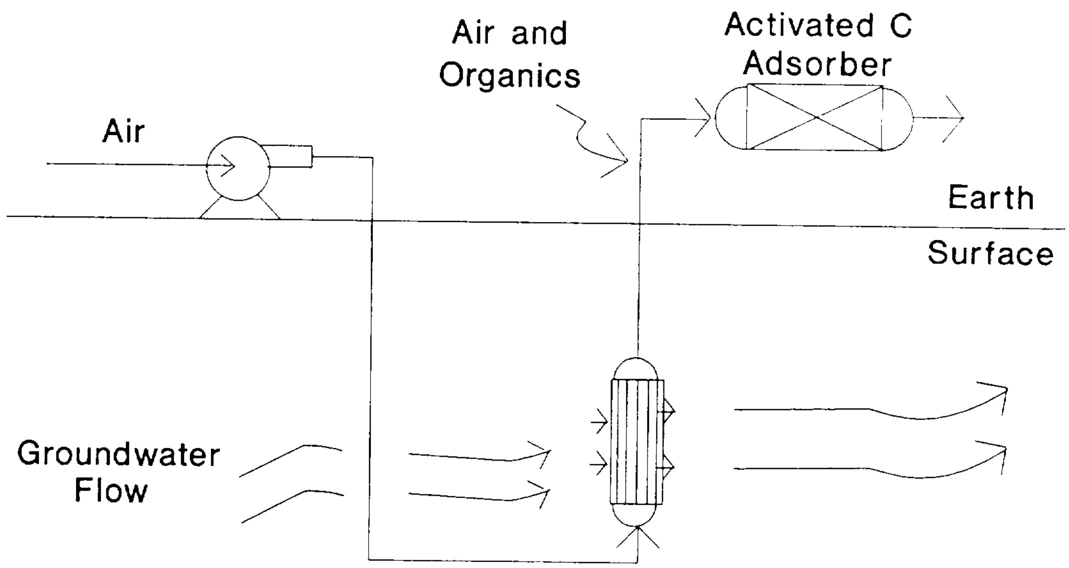


Figure RIPT.1. Removal of Organics from Groundwater via Pervaporation

3. Partially hydrolyzed polyacrylonitrite hollow fibers for separating ethanol from water. Daicel is trying this, apparently without copolymerization.

4. Chitosan membranes for separating isopropyl alcohol solutions from clean rooms. Tokuyama Soda gets selectivities of 2,400, which are probably affected by boundary layer resistances. Silicone membranes are also being tested.

These studies of membrane chemistry do not yet seem supported by studies of molecular design.

Dr. Mizoguchi felt that Japanese work would soon progress beyond ethanol-water to trace halogenated organics, especially trichloroethylene, Japan's chief dry-cleaning solvent. Intriguingly, he also suggested burying pervaporation modules around an underground flume, and trying to strip spilled solvent from underground water. Other topics were only briefly discussed. Adsorbent chemistry seems to be primitive, as it is in the United States. Crown ethers have been studied, and pyrolyzed fibers of activated carbon have been tried for odor control. Temperature-sensitive gels like isopropylacrylamide were used to treat waste dye streams, but without success. Alternative antifouling paints for boats are being developed, which will replace current formulas that use heavy metals, especially tin. Mitsubishi Heavy Industries has used membrane contactors to treat stack gas, but no new information is available.

CONCLUSIONS

This organization has a small membrane program devoted primarily to fundamental studies on membranes. The effort is a logical outcome of RIPT's wealth of polymer information. The main thrust seems to be to develop new ways to form dense layers with widely varying permeation properties onto various substrates. Commercialization is left to industry.

APPENDIX F. SITE REPORTS - CONFERENCE

Site: **Eighth Symposium on Membrane Science and Technology**

Date Visited: June 15 and 16, 1992

Report Author: E. Cussler

ATTENDEES

JTEC:

E. Cussler

BACKGROUND

The quality of the papers seemed comparable with that at a North American Membrane Society (NAMS) meeting, and somewhat better than those at an American Institute of Chemical Engineers (AIChE) meeting. Academic authors were omnipresent, but academic-industrial collaborations appeared in about 40 percent of the papers.

An outstanding talk by S. Ono covered Ube's efforts to develop gas separation membranes. These polyimide membranes have two interesting features. First, because the polymer is insoluble in most solvents, the hollow fiber membranes are made by coextrusion, with a thin polyimide coating being simultaneously extruded on top of a support layer. While this does not seem a good route to a high flux, thin film composite, it does allow making selective hollow fibers without solvents.

The second feature of these membranes is their selectivity. These selectivities are not exceptional for H_2/CO_2 and O_2/N_2, which were two stated objectives of the work. They look better for H_20/air, in which Ube also has an interest. Ube may be three to five years behind the U.S. competition.

APPENDIX G. THE AQUA RENAISSANCE PROJECT

In 1985, the Agency of Industrial Science and Technology (AIST) of the Ministry of International Trade and Industry began a five-year research initiative entitled "New Water Treatment System." This was one of 25 projects funded by AIST between 1966 and 1989 under the larger program entitled "The National Research and Development Program - The Large-Scale Project." The New Water Treatment System initiative, later dubbed the *Aqua Renaissance '90 Project*, was funded in fiscal years 1985-1990. The total funding for the project over six years is estimated at ¥11.8 billion ($90.8 million at ¥130/$). The fiscal year 1988 budget was ¥2.189 billion, growing to ¥2.528 billion in FY 1989. Of the total FY 1989 budget, ¥377 million ($2.9 million) was allocated to special accounts, presumably earmarked for new laboratory equipment and facilities related to this research project. The remainder appears to represent expenditures on salaries and other general expenses (described by AIST as general accounts) related to the research. The structure of the Aqua Renaissance '90 Project is shown in Figure Aqua.1. Judging from this figure, it appears that some private funding and/or management input may also have been involved (see "private survey organization" and "Aqua Renaissance Research Association" in Fig.Aqua.1.). As indicated in the figure, a wide variety of Japanese government laboratories, private corporations, and private associations were involved in the management and execution of the program.

The JTEC Panel on Separation Technology in Japan was asked to review the status and achievements of the Aqua Renaissance Project. Unfortunately, by the time of the panel's visit to Japan, funding had been terminated. A request to visit one of the laboratories funded under this initiative proved impossible because the laboratory had already been dismantled. Thus, information provided on Aqua Renaissance in this appendix is based primarily on previous studies that several of the JTEC panelists had been involved in (DOE 1990), on Japanese government documents in the JTEC library (MITI 1989), and on informal comments received by this JTEC panel during the course of its visits to other laboratories in Japan.

One major objective of the Aqua Renaissance Project was to find ways to treat wastewater from a variety of sources in a manner that required less land and energy than conventional approaches. Both land and energy are at a premium in Japan. The project approached this problem through a combination of anaerobic digestion and membrane concentration. In addition to wastewater treatment, the project also focused on the objective of encouraging the re-use of water (in conjunction with another MITI initiative, the Water Re-Use Promotion Center). Production of energy as a biproduct was also an objective.

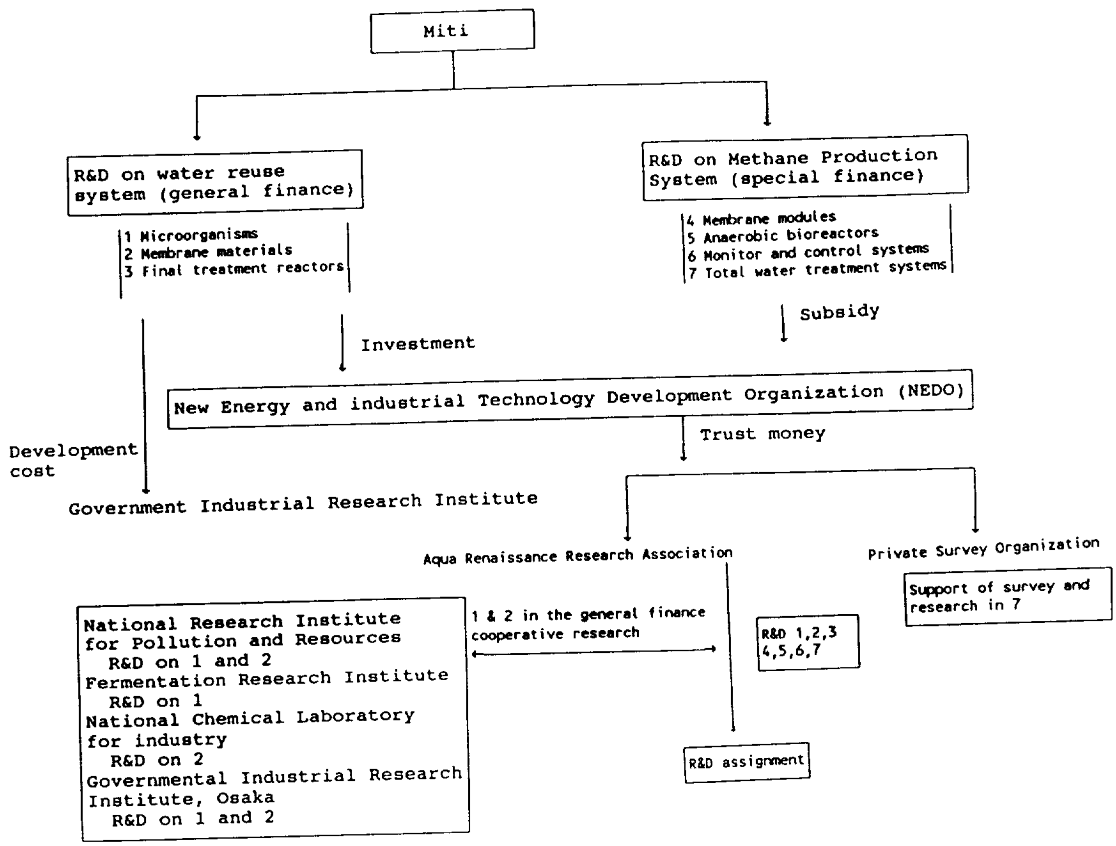
At the time the DOE Membrane panel visited Japan in 1989, the Aqua Renaissance Project had seven bench-scale field tests underway:

- large-scale municipal sewage;
- small-scale sewage (rural);
- removal of fat, oil, and protein;
- removal of wheat starch;
- removal of alcohol fermentation effluent;
- removal of pulp and paper residues; and
- night soil treatment.

William Eykamp, a member of both the 1989 DOE study team and the current JTEC panel, reports that *some* of the equipment seen in 1989 at the rural sewage field test in Chigasaki City was very impressive. This plant had originally been designed to produce methane as a major product. But by the time of the 1989 visit, this had been deemphasized; the methane was used only to heat up the feedstock to increase the rate of biological activity. The 1992 JTEC team asked to revisit this site, and was informed that this project was no longer in operation.

Several of the other six field tests had experienced similar disappointments by the time of the 1989 visit. In 1992 the JTEC panel reported little trace of the Aqua Renaissance Project. Three different Japanese hosts stated bluntly (though in confidence) that the project was a failure, and seemed to be scornful of its achievements.

Thus, the Aqua Renaissance Project obviously had its detractors in Japan, and it may not have achieved its technical objectives. However, there were some significant benefits to Japan resulting from the program: interaction between competing companies was facilitated, developing business and technical relationships that would not have existed otherwise. Furthermore, some of the project teams generated commercially useful equipment, designed for a particular need of the Aqua Renaissance Project, but useful elsewhere. Researchers who were sent to work on the project brought back knowledge to their home institutions. Thus, many Japanese companies benefitted from the cross-fertilization of ideas that took place during the Aqua Renaissance Project. This made them tougher competitors in the global marketplace.



R&D on microorganisms	Cooperative Research (Fermentation Research Institute - Aqua Renaissance Research Association)
R&D on membrane materials	Cooperative Research (National Research Institute for Pollution and Resources. Government Industrial Research Institute. Osaka - Aqua Renaissance Research Association
R&D on water treatment reactors	Japan Organo Co., Ltd., Hitachi Plant Engineering & Construction Co., Ltd.
Development of membrane separation modules for methane fermentation	Kubota, Ltd., Kurita Water Industries, Ltd., TOTO Ltd., Nitto Denko Corporation, NGK Insulators, Ltd., Mitsubishi Rayon Engineering Co., Ltd.
Development of new bioreactors for methane fermentation	Ishikawajima Harima Heavy Industries Co., Ltd., Ebara Corporation, Kawasaki Heavy Industries, Ltd., Kobe Steel, Ltd., Sanki Engineering Co., Ltd., Shimizu Corporation, Chiyoda Corporation, DIC-Degremont Co., Ltd., Nishihara Environmental Sanitation Research Corporation, Nippon Petroleum Refining Co., Ltd.
Development of an instrumental control system for methane fermentation	Toshiba Corporation, Mitsubishi Electric Corporation
Comprehensive investigation of methane fermentation	Water Re-use Promotion Center, Bioindustry Development Center (BIDEC)

Figure Aqua.1. Aqua Renaissance '90 Project R&D Organization.

REFERENCES

U.S. Department of Energy. 1990. *Membrane Separation Systems -- A Research Needs Assessment.* DOE/ER/30133-H1.

Ministry of International Trade and Industry. 1989. *Agency of Industrial Science and Technology 1989* (brochure).

ORIGINAL PAGE IS OF POOR QUALITY

APPENDIX H. GLOSSARY

BOD	Biological Oxygen Demand
BSA	Bovine Serum Albumin
DSC	Differential Scanning Calorimeter
HPLC	High Pressure Liquid Chromatography
MIBK	Methylisobutylketone
ppb	Parts Per Billion
ppm	Parts Per Million
PSA	Pressure-Swing Adsorption
RO	Reverse Osmosis
RLE	Roast-Leach-Electrowin
SEM	Scanning Electron Microscope
SFE	Supercritical Fluid Extraction
TOC	Total Organic Carbon
TOH	Total Organic Halides
TPD	Tons Per Day
UF	Ultra Filtration
ZPC	Zero Point of Charge

JTEC\WTEC reports are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161 (703) 487-4650. Prices are as of 12/92 and subject to change. Add postage plus $3.00 for handling per order, not per report. Add $7.50 for billing if order is not prepaid. These prices are for the U.S., Canada and Mexico. For information via Fax (703) 321-8547.

Title/Order Number

JTECH Panel Report on Computer Science in Japan
(12/84) PB85-216760
E06/E01 ($25.50/12.50)*

JTECH Panel Report on Opto and Microelectronics
(5/85) PB85-242402
E10/E01 ($38.00/12.50)

JTECH Panel Report on Mechatronics
in Japan (6/85) PB85-249019
E04/E01 ($20.50/12.50)

JTECH Panel Report on Biotechnology
in Japan (5/86) PB85-249241
E07/E01 ($28.50/12.50)

JTECH Panel Report on Telecommunications
Technology in Japan (5/86) PB86-202330/XAB
E08/E01 ($32.00/12.50)

JTECH Panel Report on Advanced Materials (5/86)
PB86-229929/XAB
E08/E01 ($32.00/12.50)

JTECH Panel Report on Advanced Computing in
Japan (12/87) PB88-153572/XAB
E04/A01 ($20.50/9.00)

JTECH Panel Report on CIM and CAD for
the Semiconductor Industry in Japan (12/88)
PB89-138259/XAB
E07/A01 ($28.50/9.00)

JTECH Panel Report on the Japanese Exploratory
Research for Advanced Technology (ERATO)
Program (12/88) PB89-133946/XAB
E09/A01 ($35.00/9.00)

JTECH Panel Report on Advanced Sensors in Japan
(1/89) PB89-158760/XAB
E11/A01 ($41.00/9.00)

JTEC Panel Report on High Temperature
Superconductivity in Japan (11/89)
PB90-123126
E10/A02 ($38.00/12.50)

JTEC Panel Report on Space Propulsion in Japan
(8/90) PB90-215732
E10/A02 ($38.00/12.50)

JTEC Panel Report on Nuclear Power in Japan
(10/90) PB90-215724
A14/A02 ($52.00/12.50)

JTEC Panel Report on Advanced Computing in Japan
(10/90) PB90-215765
A10/A02 ($36.50/12.50)

JTEC Panel Report on Space Robotics in Japan (1/91)
PB91-100040
E14/E01 ($52.00/12.50)

JTEC Panel Report on High Definition Systems in
Japan (2/91) PB91-100032
E14/E01 ($52.00/12.50)

JTEC Panel Report on Advanced Composites in Japan
(3/91) PB90-215740
E10/E01 ($38.00/12.50)

JTEC Panel Report on Construction Technologies in
Japan (6/91) PB91-100057
E14/E01 ($52.00/12.50)

JTEC Program Summary (9/91)
PB92-119429/XAB
E10/E01 ($38.00/12.50)

JTEC Panel Report on X-Ray Lithography in Japan
(10/91) PB92-100205
E10/E01 ($38.00/12.50)

WTEC Panel Report on European Nuclear
Instrumentation and Controls (12/91)
PB92-100197
E14/E04 ($52.00/20.50)

JTEC Panel Report on Machine Translation in Japan
(1/92) PB92-100239
E10/E02 ($38.00/15.50)

JTEC Panel Report on Database Use and Technology
in Japan (4/92) PB92-100221
E10/E02 ($38.00/15.50)

JTEC Panel Report on Bioprocess Engineering in
Japan (5/92) PB92-100213
E14/E04 ($52.00/20.50)

JTEC Panel Report on Display Technologies in Japan
(6/92) PB92-100247
E14/E04 ($52.00/20.50)

JTEC Panel Report on Material Handling
Technologies in Japan (2/93)
PB93-128197

JTEC Panel Report on Separation Technology in
Japan (3/93) PB93-159564

*The first code and price are for hardcopy; the second for microfiche.